

PA 36/49T14

KURSANOV, D. N.

USSR/Chemistry - Alcohols, Reactions of Sep 48
With Allyl Pyridine Chloride
Chemistry - Alkoxy Groups

"The Interaction of Allyl Pyridine Chloride and
Alcohol," D. N. Kursanov, O. M. Shemyakina, Inst
Org Chem, Acad Sci USSR, Moscow Textile Inst,
3 pp

"Dok Ak Nauk SSSR" Vol LXII, No 3

It has been established that an alkoxy-methyl
radical changes places easily with hydrogen in
the hydroxy group, resulting in transformation
of alcohols. Attempts to find if this reaction
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USSR/Chemistry - Alcohols, Reactions of Sep 48
With Allyl Pyridine Chloride
(Contd)

can be extended to quaternary salts of ammonia
with other radicals. Finds that allyl radical
and alkoxy-methyl radicals of quaternary ammonia
salts behave in the same fashion during inter-
action with alcohols. However, in this case,
yield was only a little over 10% of the theoret-
ical. Submitted by Acad B. A. Kuznetsov,
13 Jul 48.

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Exchange reactions and cleavages of the quaternary ammonium salts. II. Reaction of quaternary ammonium salts of the type $ROCH_2N^+X^-$ with carboxylic acids and their salts. V. N. Setkina and D. N. Kursanov. *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1940, 100-7; *cf. C.A.* 42, 4925. Quaternary ammonium salts containing the $ROCH_2$ radical react with salts of carboxylic acids, yielding alkoxymethyl esters, while the free acids yield esters without the alkoxymethyl group, the CH_3O residue being eliminated as polyoxymethylene. Heating 25.2 g. 1-(butoxymethyl)quinolinium chloride and 8.2 g. dry $NaOAc$ 3 hrs. at $150-170^\circ$ gave 72% $BuOCH_2OAc$, b_p 118-119°, b_r 167.8°, d_4^{20} 0.9328, n_D^{20} 1.4040, and quinoline. Similarly, 1-(decyloxymethyl)pyridinium chloride at $180-200^\circ$ gave 60% *decyloxymethyl acetate*, b_p 167.5°, d_4^{20}

0.9072, n_D^{20} 1.4301. 1-(Tetradecyloxymethyl)pyridinium chloride similarly ($150-60^\circ$) gave 70% *tetradecyloxymethyl acetate*, b_p 211°, d_4^{20} 0.8960, n_D^{20} 1.4390. Heating 13.8 g. 1-(butoxymethyl)quinolinium chloride with 6.2 g. $PrCO_2Na$ 2 hrs. to $150-50^\circ$ at a water-pump vacuum gave 75% $PrCO_2CH_2OBu$, b_p 81°, d_4^{20} 0.9290, n_D^{20} 1.4147, while $AmCO_2Na$ at $190-200^\circ$ gave 69% $AmCO_2CH_2OBu$, b_p 132.5°, d_4^{20} 0.9121, n_D^{20} 1.4210, from 1-(butoxymethyl)pyridinium chloride; the latter and $NaOBz$ at $180-200^\circ$ at a water-pump vacuum gave $BzOCH_2OBu$, b_p 158°, d_4^{20} 1.0440, n_D^{20} 1.4930. Substitution of 1-(decyloxymethyl)pyridinium

chloride ($200-30^\circ$) in the above gave 54% *decyloxymethyl benzoate*, b_p 223.5°, d_4^{20} 0.9511, n_D^{20} 1.4778. 1-(Butoxymethyl)pyridinium chloride (14.2 g.) and 6.1 g. $PhCHCl_2$ after 3 hrs. at $130-40^\circ$ gave 57% $PhCH_2CO_2CH_2OBu$, b_p 133°, b_r 167.5-8.5°, d_4^{20} 1.0500, n_D^{20} 1.4981. Hydrolysis of the products by dil. HCl gave ROH , CH_3O , and the corresponding acids. Heating 22.5 g. 1-(butoxymethyl)quinolinium chloride and 5 g. $AcOH$ to $150-50^\circ$ 7 hrs. gave 57% $BuOAc$, while $PrCO_2H$ at $150-60^\circ$ gave $PrCO_2Bu$. 1-(Decyloxymethyl)pyridinium chloride and $AmCO_2H$ at $150-60^\circ$ gave 28% $AmCO_2C_{10}H_{21}$, b_p 183.1°, n_D^{20} 1.4351, d_4^{20} 0.9010, 22% $C_{17}H_{35}OCH_2PhC_6H_5$, b_p 213-14°, d_4^{20} 0.8908, n_D^{20} 1.4305, and 2.5 g. $(C_{10}H_{21}O)_2CH_2$, b_p 202.5°, d_4^{20} 0.8451, n_D^{20} 1.4100 (the previous derivs. gave CH_2O polymers on distn.). 1-(Butoxymethyl)quinolinium chloride and $PhCH_2CO_2H$ in 6 hrs. at $160-80^\circ$ gave $PhCH_2CO_2Bu$, b_p 138-40°, d_4^{20} 0.9280, n_D^{20} 1.4908 (65%). Heating 1-(butoxymethyl)quinolinium chloride with $AcOH$ in Ac_2O (to insure anhyd. conditions) 5 hrs. at $150-60^\circ$ and 8 hrs. at $160-80^\circ$ gave 61% $BuOAc$, $BuOCH_2OAc$ (17 g.) and 18 g. $AcOH$ heated 1.5 hrs. at $195-200^\circ$, with recovery of the volatiles, gave CH_2O (detected as the dimethyl deriv., m. 180°), 30% $BuOAc$, and 11 g. starting ester.

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Exchange and cleavage reactions of quaternary ammonium salts. III. Reaction of quaternary ammonium salts with esters. D. N. Kursunov and V. N. Setkina. *Invest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1949, 274 8. *ibid.* C.I. 43, 6666. 1-(Butoxymethyl)quinolinium chloride (10 g.) and 2 g. EtOAc in 5 hrs. at 150-5° give 10 g. EtOAc and 3.0 g. BuOAc (60%), as well as some quinoline. 1-(Diethylamino)pyridinium chloride (10 g.) and 120 g. EtOAc in 10 hrs. at 195-205° gave 100 g. EtOAc and 82.5% diethyl acetate, b.p. 118-19°, n_D²⁰ 1.4272. EtOH (32.3 g.) and 28.4 g. 1-benzylpyridinium chloride in 8 hrs. at 195-205° give 4 g. pyridine, 1.5 g. BaOH, and 60% BaOCH₂Ph. The reaction probably proceeds by

formation of an oxonium deriv. at the O of the ester after cleavage of the R group from the quaternary compound. IV. Mechanism of the reactions of quaternary ammonium salts with alcohols. V. N. Setkina and D. N. Kursunov. *Ibid.* 311 16. Pyridine MeI (37 g.) and 24.8 g. decanol in 12 hrs. at 190-220° gave 28% decene, b.p. 167°, 18%; Me decyl ether, b.p. 91-5°, d₄²⁰ 0.8222, n_D²⁰ 1.4240, and 32% decyl ether, b.p. 180-7°, d₄²⁰ 0.8188, n_D²⁰ 1.4114. Octanol similarly gave in 6 hrs. at 210-300° 1.2% octene, b.p. 122°, 10%; Me octyl ether, b.p. 170-2°, d₄²⁰ 0.8145, n_D²⁰ 1.4160, and decyl ether, 54%, b.p. 117-5-8.5°, d₄²⁰ 0.8065, n_D²⁰ 1.4327. Heating 0.5 g. 1-(diethylamino)pyridinium chloride and 18.4 g. PhCH₂OH 4 hrs. at 180-200° gave 20% HCH(OH)Ph, 11%; BuOCH₂Ph, 0.2%; BuO(PhCH₂O)CH₂Ph, b.p. 118-19°, d₄²⁰ 0.9654, n_D²⁰ 1.4830, and 4.4 g. (PhCH₂)₂O; the residue contained benzylpyridinium ion, shown by the *paraffin*, m. 117-18°. The results are discussed in terms of formation of the products through oxonium derivs. formed from radical cleavage of the quaternary salts. G. M. K.

Influence of the structural factors on conjugation phenomena. I. Mobility of hydrogen atoms in various cyclic ketones. A. N. Nesmeyanov, D. N. Kursanov, K. A. Pecherskaya, and Z. N. Parnes (Inst. Org. Chem., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1949, 592-7. — 2,2,6-Trimethylcyclohexanone completely exchanges one H for a D atom after 70 hrs. at 130° in enriched H₂O; cyclohexanone exchanges 4 H atoms for D atoms in 50 hrs. at 100°. Spiro[4.5]decane-6-one exchanges between 1 and 2 H atoms for D in 70 hrs. at 130°. No exchange takes place with camphenilone or camphorquinone; this is explained by nonexistence of conjugation between the CO group and CH, which follows from Bredt's rule. II. Mobility of hydrogen atoms in acetylacetone and its cobalt and aluminum salts. A. N. Nesmeyanov, D. N. Kursanov, T. A. Smolina, and Z. N. Parnes. *Ibid.* 598-600. — CH₃Ac, kept 70 hrs. at 17° in H₂O enriched with D₂O in the presence of dioxane showed exchange of 2 H (within 13%) for 2 D. The Co salt and the Al salt show no enrichment by D. The result is explained on the basis of impossibility of conjugation of the residual CH bond with CO due to perpendicularity of the axes of the CH link and that of the π -function of the CO group, as well as to Favourskii's rule (*C.A.* 35, 2840⁹), which forbids allene formation in 6-member rings. G. M. K.

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Reaction of quaternary ammonium salts with ethers
 D. N. Kursanov and V. N. Setkina. *Doklady Akad. Nauk S.S.S.R.* 65, 847-50 (1949). EtOCH_2Ph (3.0 g) and 20.5 g. 1-benzylpyridinium chloride after 6 hrs. at 180° gave 8.7 g. unreacted ether and 18.5% $(\text{PhCH}_2)_2\text{O}$, b.p. 172° , and the acidic ext. gave 1-benzylpyridine, isolated as the picrate, m. $137-8^\circ$. Bu_4O (15.5 g) and 1-(decyloxymethyl)pyridinium chloride (10 g) in 5 hrs. at $180-200^\circ$ gave 11.8 g. unreacted Bu_4O , 1.0% decyl chloride, b.p. $105-5.5^\circ$, 9.4% $\text{C}_{10}\text{H}_{21}\text{O}(\text{Bu})\text{CH}_2$, b. $118-50^\circ$, d_4^{20} 0.8472, n_D^{20} 1.4120, and 55.5% $\text{C}_{10}\text{H}_{21}\text{O}(\text{C}_6\text{H}_5)\text{CH}_2$, b. 208° , d_4^{20} 0.8451, n_D^{20} 1.4410. Similarly $\text{PhCH}_2\text{N}^+\text{PhMe}_3\text{Cl}^-$ and Bu_4O gave under the above conditions 1.0% $(\text{PhCH}_2)_2\text{O}$ and 25% *p*-benzyl *N,N*-dimethylamine, b. $180-1^\circ$, d_4^{20} 1.0120, n_D^{20} 1.0001. PhOMe and 1-benzylpyridinium chloride in 8 hrs. at $180-200^\circ$ gave 1.0% $(\text{PhCH}_2)_2\text{O}$, b. 107° , and 8% of mixed 4-hydroxydiphenylmethane, m. $82-2.5^\circ$, and 4-methoxydiphenylmethane, m. 81° ; the acid ext. contained 1-benzylpyridine, identified as the picrate, m. 138° . The use of PhOH in the above gave 8.2% PhOCH_2Ph and 10% mixed 4-hydroxydiphenylmethane and the 1-EtO deriv., as well as a little PhOH .
 G. M. Kosolapoff

ASH-SLA METALLURGICAL LITERATURE CLASSIFICATION

Exchange reactions and cleavages in the quaternary ammonium salt group. VI. Reaction of salts of alkoxymethylpyridinium with phenols. V. N. Setkina and D. N. Kurzinov. *Izv. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, 1950, 350-351; cf. *Chim.* 42, 4024; 44, 9337. Phenols and alkoxymethylpyridinium salts yield, as primary products, phenyl alkyl formals; secondary reactions yield dialkyl formals, phenolformaldehyde resins, and aliphatic alcs. The dialkyl formals react with ArOH, yielding ROH and the resins. $(PhO)_2CH_2$ appears to react with pyridine-HCl via an ion-chain reaction mechanism, yielding protonated adducts which cleave into PhOH and $PhOCH_2^+$ ions, the latter carrying the chain reaction that yields the resin by successive addn. of H ion. Heating 43.2 g. 1-(butoxymethyl)pyridinium chloride and 25.2 g. PhOH 70 min. to 100-60° gave 9.4 g. (50%) $(BuO)_2CH_2$, 14.6% $BuOCH_2Ph$, bp 127-8°, d_4^{20} 0.9752, n_D^{20} 1.4890, 70% resin, and an unstated amt. of pyridine-HCl; 6 hrs. at 180-5° gave 15% $BuOH$, 57% $(BuO)_2CH_2$, some pyridine, and 80.7% resin. 1-(decyloxymethyl)pyridinium chloride yielded, similarly, in 1 hr. at 130-50° 5% PhOH, 5% decyl chloride, 4.8% decyl alc., 30% *decyl Ph formal*, bp 187.5-8.0°, n_D^{20} 1.3780, d_4^{20} 0.9259, 57.5% *didecyl formal*, bp 208-10°, n_D^{20} 1.4118, d_4^{20} 0.8168, and 62% resin. 1-(Tetradecyloxymethyl) analog gave 92% *ditetradecyl formal*, m. 12-2.5°, and 80% resin. 2-Naphthol (8 g.) and 10.2 g. 1-(tetradecyloxymethyl)pyridinium chloride in 10 hrs. at 150-60° gave 98% *ditetradecyl formal*, pyridine-HCl, and an unstated yield of resin; 1-naphthol gave 90% of the above

formal and an alkali-sol. resin. Heating 4.5 g. PhOH and 20 g. $(BuO)_2CH_2$ 3.5 hrs. at 160-90° gave 68% $BuOH$ and 4 g. phenolformaldehyde resin; 2-naphthol reacted similarly. Heating 3.9 g. PhOH and 10 g. *didecyl formal* 6 hrs. at 180-200° gave 8 g. *decyl alc.* (83°C), bp 146°, n_D^{20} 1.4378, d_4^{20} 0.8136, and 2.6 g. NaOH-insol. resin. The absence of $(PhO)_2CH_2$ in the products is explained by the following fact: heating this formal (10 g.) with 2.5 g. pyridine-HCl 10 hrs. at 195-202° gave 1.5 g. NaOH-sol. resin, 36% PhOH, and 4.7 g. resinous residue after distn. of the PhOH.

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Effect of structural factors on conjugation phenomena.
III. Mobility of hydrogen atoms in the dibenzoylmethane molecule. D. N. Kuranov, Z. N. Parnes, and T. A. Simolova. *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1950, 512-17; cf. C.A. 44, 3917d. Heating Bz_2CH_2 with H_2O enriched with D_2O 25 hrs. at 19° gave no D-H exchange, but in dioxane- D_2O an exchange of 1 H readily took place after 20 hrs. at 0° ; at 17° or 40° somewhat over 1 H is exchanged, and at 150° almost 2 H exchange occurs. Ph_2NH gives similar results. Stearic acid, myristic acid, and fumaric acid give only fractional exchange with D_2O alone, but on addition of dioxane the exchange is nearly complete. The results are interpreted as being the consequence of essential mobility of the given compounds in H_2O alone. G. M. K.

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Exchange and cleavage reactions of the quaternary salts of ammonium. VII. Reaction of salts of (alkoxymethyl)pyridinium with alkyl ethers of phenols. D. N. Kursanov and V. N. Setkina. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1950, 654-8; cf. C.A. 45, 6201g. — Heating 28.3 g. 1-(decyloxymethyl)pyridinium chloride with 38.8 g. EtOPh 8 hrs. to 180-95° (sealed tube) gave 29 g. EtOPh, 1 g. decyl chloride, 4.6 g. decyl alc., bp 125°, n_D^{20} 1.4378, d_4^{20} 0.8340, 2 g. $\text{PhOCH}_2\text{OC}_6\text{H}_5$, bp 200-5°, n_D^{20} 1.4768, d_4^{20} 0.9210, and 7 g. $(\text{C}_6\text{H}_5\text{O})_2\text{CH}_2$, bp 232-4°, n_D^{20} 1.4420, d_4^{20} 0.8462; some 5.2 g. (38%) phenol-formaldehyde resin was secured from the residues. (Butoxymethyl)pyridinium chloride (20.1 g.) with 19.8 g. MeOPh 6 hrs. at 190-5° gave 1.4 g. BuOH, 1.1 g. $(\text{BuO})_2\text{CH}_2$, bp 178-82°, b, 62°, n_D^{20} 1.4076, d_4^{20} 0.8580, 1.1 g. unknown substance, bp 45-75°, and 7.7 g. (10%) phenol-formaldehyde resin. Heating 10 g. $(\text{C}_6\text{H}_5\text{O})_2\text{CH}_2$ with 3.9 g. PhOH 6 hrs. to 180-200° gave 8 g. decyl alc. and 2.6 g. solid which was elastic at first, then hardened on attempted distn., i.e. a form of phenol-formaldehyde resin. Hence, the pyridinium salts undergo transetherification with the phenol ethers, yielding formaldehyde, which symmetrizes and then reacts with the formation of the polymeric resins. The reaction of phenols and of their ethers with salts of (alkoxymethyl)pyridinium ion are analogous. G. M. Kozlov

KURSANOV, D.N., KABACHNIK, M.I., KAVERZNEVA, Ye.D., PRILEZHAYEVA, Ye. N., SOKOLOV, N.D.
and FREYDLINA, R. Kh.

"The Current State of the Theory of Chemical Structure," Usp. Khim.,
19, No.5, pp 529-544, 1950

Translation W-16104, 30 Dec 50

KURSANOV, D. N.

N. N. Mel'nikov, A. S. Zabrodina, D. N. Kursanov, and A. K. Ruzhentseva

"S. S. Nametkin's Work in the Field of Petroleum Chemistry," Uskhi Khimii, Vol. XIX,
No. 6, 1950, pp. 657-672

KURSANOV, D.N.

✓ Influence of the structural factors on configuration phenomena. I. Mobility of hydrogen atoms in cyclic ketones of different structures. A. N. Nesmeyanov, D. N. Kurayov, K. A. Pecherskaya, and E. N. Farnes. Uchenye

Zapiski Akad. Nauk SSSR, *Chem. Ser.*, 1956, 10, 1037-1040. (1956)
No. 132, Org. Khim., 7, 56-61 (1956).—See C.A. 44, 3917s.
11. Reactibility of hydrogen atoms in acetylacetonates and cobalt and aluminum acetylacetonates. A. N. Nemeyanov, D. N. Kurzanov, T. A. Smolina, and Z. N. Farnes. *Ibid.* 62-66. 62-66.—See C.A. 44, 3917s. IV. Reactivity of α -C \equiv C link of ketones of different configurations. A. N. Nemeyanov, K. A. Pecherikaya, and T. P. Tolstaya. *Ibid.* 66-72; cf. C.A. 45, 6106a. —To 54 g. μ -[4,5]decan-4-one in 150 ml. Et $_2$ O was slowly added 14.7 g. powd. NaNH $_2$; after heating to expel all NH $_3$, the soln. was treated with 53 g. MeI, acid., with H $_2$ O, and the org. layer sepd. and washed; distn. gave 37% 7-methylspiro[4.5]decan-6-one (II), bp 101-2°, n_D^{20} 1.440, d_4^{20} 0.8813. This (5 g.) in Et $_2$ O was treated with 7.8 g. diazox-Br in Et $_2$ O and after 2-3 min. the colorless soln. was washed with Na $_2$ CO $_3$ and distd., yielding 0.2 g. unreacted material and 50% 7-bromo deriv. (I), bp 100-1°, n_D^{20} 1.5210, d_4^{20} 1.3270. Similar reaction of 7 g. spiro[4.5]decan-6-one with 11.3 g. diazox-Br gave 72% 7-bromospiro[4.5]decan-6-one, m. 47-8°, which decarbox. on exposure to air yielding iHBr. 1,1,6-Triaethyl-1-cyclohexanone, b. 178.5-0.6°, n_D^{20} 1.4193, with 6.5 g. diazox-Br similarly gave 80% 6-bromo deriv., m. 37-8°. Camphenylene failed to react with diazox-Br after 2 hrs. refluxing in Et $_2$ O. I (3.30 g.) and 0.34 g. Me in Et $_2$ O yielded a Grignard reagent which treated with CO $_2$ gave 61% methylspirodecanone, b. 85°, n_D^{20} 1.4830. Addn. of 0.28 g. CS(NH $_2$) $_2$ to 1.15 g. 7-bromospiro[4.5]decan-6-one followed by warming led to a vigorous reaction which was accompanied by gas evolution; treatment of the cooled clear mass with 0.075 g. NaOH gave 30% 7-methylspiro[4.5]decan-6-one.

m. 120-30° (from EtOH). II (1 g.) shaken with 1.47 g. dioxane-SO₂ in (CH₃Cl)₄ and left overnight, then treated with aq. BaCO₃ boiled to expel the org. solvent, filtered and evapd. gave 88% Ba 1-sulfonate dihydrate, sol. in H₂O and warm PhMe. Similarly was obtained 90% 2,2,6-trimethyl-1-cyclohexanesulfonic acid, isolated as Ba salt, dihydrate, sol. in H₂O and warm PhMe. Camphenylene failed to react with dioxane-SO₂. II (2 g.) in 1 ml. concd. HCl was reactd with dioxane-SO₂. II (2 g.) in 1 ml. concd. MeONO treated with ice cooling with a slow stream of MeONO over 6 hrs.; a green color developed along with sepn. of 0.3 g. colorless 7-nitroso-II, m. 111-12° (from CHCl₃-petr. ether). Similar reaction of 2,2,6-trimethyl-1-cyclohexane run at 45-7° gave 35% 6-nitroso deriv., decomp. 113-135°. Camphenylene failed to react with MeONO. The lack of reactivity of this substance is ascribed to impossibility of conjugation between the CO and the adjacent C1 link.

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Exchange and cleavage reactions of quaternary ammonium salts. VIII. Reaction with alcohols and phenols of substituted ammonium salts with a benzyl radical. V. N. Setkina and D. N. Kirsanov. *Izvest. Akad. Nauk S.S.S.R., Khim. Khim. Nauk* 1951, 81-5; cf. C.I. 45, 0201g, 8220h. - Quaternary ammonium salts contg. benzyl radicals form with alcs. or phenols benzyl ethers of the corresponding alcs. or products of exchange of the mobile H of the phenols for the PhCH_2 group both in the OH group as well as in the ortho and para positions; with naphthols the reaction is predominantly nuclear substitution in the ortho and para positions with respect to OH. Heating 15 g. $\text{PhCH}_2\text{NMe}_3\text{PhCl}$ and 9 g. AmOH 5 hrs. at $140-55^\circ$ gave 6.4 g. PhCH_2OAm , bp $116-17^\circ$, d_4^{20} 0.9142, n_D^{20} 1.4851. Similarly, 13.4 g. 1-benzylpyridinium chloride (I) and 10 g. CulnOH 8 hrs. at $160-80^\circ$ gave 7 g. $\text{PhCH}_2\text{OCuln}$, bp $177-8^\circ$, d_4^{20} 0.8884, n_D^{20} 1.4770. 2-CulnOH (24.4 g.) and 41.2 g. I in 6 hrs. at 180° gave a wide series of fractions: 12% unreacted naphthol, 60% 1-benzyl-2-hydroxynaphthalene, m. $111-11.5^\circ$ (from 80% HCO_2H), bp $225-42^\circ$ (crude), and 1.2 g. CulnO , m. $180.5-90.0^\circ$,

whose structure is unknown. Similarly, 28.8 g. 1-CulnOH and 41.2 g. I in 6 hrs. at $180-200^\circ$ gave 29.5% unreacted naphthol, 31% 1-hydroxy-4-benzynaphthalene, bp 227° , m. 125.5° , and 9.5 g. viscous oil, bp $210-310^\circ$, composed of several products from which an extr. with ligroine gave 1 g. CulnO , m. 72° , identified as 1-hydroxy-2,4-dibenzynaphthalene. Heating 18.8 g. PhOH with 41 g. I 6 hrs. at $180-200^\circ$ gave 25% PhOH , 18% PhOCH_2Ph , m. 39° , bp $143-6^\circ$, 18% mixed isomeric benzyl ethers of benzylphenols, bp $250-45^\circ$, 20% almost pure *p*-benzylphenol, m. 84° , and 17% mixed *o*-benzylphenols, bp $245-52^\circ$. G. M. Kosolapoff

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1957 AND 1958 EDITIONS

PROCESSES AND PROPERTIES WITH

MAGYAR KIMIAI FOLYOIRAT
HUNGARIAN JOURNAL OF CHEMISTRY
VOL 57, —1951
No. 2, Feb.

D. M. Kurepaev
and associates:
On the question of the present state
of the theory of chemical structure
(From the Russian) 51-61

ADD TO A DETAILING LITERATURE CLASSIFICATION

1957 AND 1958 EDITIONS

1957 AND 1958 EDITIONS

KURSHANOV

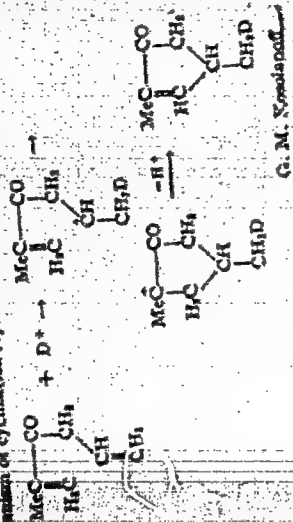
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8
RmL

Reaction mechanism of the cyclization by means of
dentation. I. Cyclization of isopropenyl allyl ketone.
D. N. Kurshov, Z. N. Parnes, I. I. Zaretskaya, and I. N.
Kuznetsov. Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.
1953, 103-7 (Engl. translation).—See C.A. 48, 3271g.
H. L. H.

3-1-55
RmL

KUR SANOV, D.N.

Reaction mechanism of the cyclization by means of
deuterio. 1. Cyclization of isopropyl allyl ketone,
D. N. Kurzanov, Z. N. Parnes, I. I. Zariakaya, and I. N.
Kurzanov, *Zh. Fiz. Khim.*, 1953, 27, 114-20. *Chem. Abstr.*
48:114-20. 114-20. Cyclization of $\text{CH}_3\text{CH}(\text{CH}_3)\text{CO}-$
 CH_2CH_3 (I) was studied in the presence of H_2PO_4 , en-
riched with D (d. 1.70). I and I part catalyst were kept
2-3% but at 10-24°, the exchange of D between the catalyst
and the I cyclization product is very extensive; being some-
what lower that required for exchange of 1 H by 1 D in 20
hrs. at 19°. Fractionation of the product gave dimethyl-
cyclopentanone, b.p. 77-78°, n_D^{20} 1.4670, d_4^{20} 0.8387. The
results clearly show that the cyclization is accompanied by
introduction of 1 D atom, confirming the Nazarov mecha-
nism of cyclization represented below:



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Apr. 10, 1954
Organic Chemistry

High-molecular compounds. Li. Exchange reaction in polyesters studied by means of the heavy isotope of hydrogen. D. N. Kurbanov, V. V. Korshak, and M. V. Vinogradov. *Dokl. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 140-4; cf. *C.A.* 46, 1446t, 7637d, 48, 2692. In polyesterification reactions it was shown that ester interchange reactions take place. Hydrogenation of *o*-Et maleate with D-enriched H over Pd gave di Et (50% CCHD), contg. some 21% of the theoretical content of D. This was heated with polyhexamethylene sebacate in the molten state 10 hrs. at 250° and the polymer was isolated and examined for D content by the usual combustion method. Some 34% exchange took place under the above conditions, with an original ratio in the mixt. of 1 mole deuterio ester-chain unit $[-O(CH_2)_4OCO(CH_2)_4CO-]$ of the polyester chain.

G. M. Kamolapoff

KURSAV, B. N.

The mechanism of the cyclization reaction by means of deuterium. II. I. N. Nazarov, I. I. Zaretskaya, Z. N. Barnes, and B. N. Kursav. *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk* 1953, 519-23; cf. C.A. 48, 3271c. — It was previously shown that cyclization of 2-methyl-1,5-hexadien-3-one in D-enriched H_2PO_4 results in the entry of D into the cyclopentenone deriv., indicating the correctness of the ionic nature of the reaction as proposed by Nazarov (C.A. 48, 811d), in which in the initial step D⁺ adds to the terminal C of the allyl group. The location of the D in the product was now investigated. The deuterio-2,4-dimethyl-2-cyclopenten-1-one, obtained as described above, was ozonized, yielding $HO_2CCHMeCH_2CO_2H$, which contained substantially all the D that was present in the cyclopentenone. Thus the presence of D on the 1-, 2-, 3-, or 4-positions is excluded. Oxidation of the cyclopentenone with SeO_2 gave D-free 2,4-dimethyl-2-cyclopenten-1,4-dione, m. 61-5°. Hence D must be present in the 5-position, i.e. the methylene group adjacent to the carbonyl. This shows that the cyclization is entered not by $CH_2:CHCH_2COCMe:CH_2$, but by its isomer, $MeCH:CH-COCMe:CH_2$. No exchange of D occurs between the cyclopentenone deriv. and $AcOH-AcOD$. G. M. K.

KURSAKOV, D.N.

USSR.

✓ Hydrogen exchange of saturated hydrocarbons in reaction with sulfuric acid. D. N. Kursakov, V. N. Setkina, and O. D. Stepanov. *Bull. Acad. Sci. Div. Chem. Sci.* 1954, 22 (Engl. translation).—See C.A. 49, 2296k. H. L. H.

KURSANOV, D. N.

USSR/Chemistry - Isotopes;
Hydrocarbons Nov/Dec 53

"Hydrogen Exchange of Saturated Hydrocarbons in the Interaction With Sulfuric Acid," D.N. Kursanov, V.N. Setkina, O. D. Sterligov, Inst Org Chem, Acad Sci USSR

Iz Ak Nauk SSSR, OZhN, No 6, pp 1035-1042

Investigated the exchange capacity of H atoms of n-heptane, n-dodecane, 2-methylpentane, 3-methylhexane, 2,2-dimethylhexane, 2,2,3-trimethylbutane, and 2,2,4-trimethylpentane in the interaction with deuteriosulphuric acid (I). 273T12

Found that only hydrocarbons that have a tertiary C atom are capable of this exchange, and that equil is established within several hours at 20-25°. Also established that the highly mobile H atoms of alicyclic hydrocarbons with tert-C atoms are exchanged for deuterium on contact with I. State that the results check with data subsequently published by USA investigators.

Reactions of hydrogen exchange of α,β -unsaturated ketones. D. N. Kuznetsov and Z. N. Parnes (Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 91: 1123-8 (1953). When various satd. ketones are heated with H_2O enriched with D_2O in dioxane in the presence of a small amt. of base (1,2-dihydro-1-methyl-2-methylimino-pyridine) exchange of D for all H atoms on α -Carbons takes place readily. However, $(PhCH=CHCO)_2$, $PhCH=CHCOCH_3$, $Me_2C=CHCOCH_3$ do not react or show at most a very minute D-H exchange. If the unsatd. links in these ketones are satd. by hydrogenation, the D-H exchange takes place readily. Thus, H atoms on α -C atoms in α,β -unsatd. ketones do not exchange if for D, as a result of suppression of carbonyl-double bond conjugation. When $Me_2C=CHCOCH_3$ or $H_3C=CHCOCH_3$ are subjected to D-H exchange, the exchange takes place readily but only at the Me groups, to which the proton mobility is transferred. $(Me)_2C=CHCOCH_3$ readily exchanges 2 H atoms for 2 D atoms, but $Me_2C=CHCOCH_3$ does not exchange H for D at all. The latter substance was prepd. from $Et_2C=CHCOCH_3$ with $NaCH_3$; bp 118-9°, d_4^{20} 1.0791, n_D^{20} 1.4485.

O. M. Kozolapoff

KUR SANOV, D. N.

USSR.

[Hydrogen exchange of cyclic saturated hydrocarbons in
reaction with sulfuric acid. V. I. Sokolov, D. N. Kur-
sanov, and A. L. Liberman. *Dokl. Akad. Nauk SSSR*,
Div. Chem. Sci. 194, 60 (1969). Translation
C.A.B. 61111.]

U.S.S.R.

KURSAKOV, D. N.

U.S.S.R.

D-Hydrogen exchange of cyclic saturated hydrocarbons in reaction with sulfuric acid. V. N. Seleznev, D. N. Kursakov, and A. L. Liberman (*Inst. Org. Chem., Acad. Sci. USSR, Moscow*). *Tr. Akad. Nauk S.S.S.R., Khim. Nauk* 1954, 109-116; cf. C.A. 49, 2298h. —D-H exchange of cyclic hydrocarbons in the presence of D-enriched H_2SO_4 was examined. The D-H exchange is entered into by monocyclic hydrocarbons which contain tertiary C atoms (methyl-, 1,1-dimethyl-, and 1-methyl-4-ethylcyclohexane, methylcyclopentane), and the equil. is established at room temp. in a few hrs. No exchange takes place with cis and trans forms of decahydronaphthalene. In mixts. of hydrocarbons which contain secondary and tertiary C atoms, only the latter react. Substantial no exchange occurs with cyclohexane. 1,1-Dimethylcyclohexane also does not react, neither does cyclopentane. When the exchange takes place, all H atoms are capable of exchange. Isomerization of substituted cyclohexanes is taken into account. G. M. Kosolapov

KURSA NOV, D. N.

a Reaction mechanism of the cyclization by means of deuterium. III. D. N. Kursanov, Z. N. Paenec, I. I. Zaretskaya, and I. M. Nazarov (N.D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izv. Akad. Nauk S.S. S.R., Otdel. Khim. Nauk* 1954, 859-64; cf. C.A. 48, 9939b. Heating $\text{Me}_2\text{C}(\text{C}(\text{CH}_3)_2)\text{COCH}_2\text{CH}(\text{OMe})\text{Me}$ with $\text{p-}62$
 $\text{Me}_2\text{C}(\text{H}_2\text{SO}_4\text{H})$ yielded $\text{Me}_2\text{C}(\text{C}(\text{CH}_3)_2)\text{COCH}(\text{CH}_3)_2$, b.p. 93-3.5°, n_D^{20} 1.4735, d_4^{20} 0.8789. This on cyclization with H_3PO_4 (cf. C.A. 44, 8907i) gave 2-isopropyl-3,4-trimethyl- β -cyclopentenone (I), b.p. 112-12.5°, n_D^{20} 1.4779, d_4^{20} 0.9245, which was then used for the study of D-H exchange by 2 hrs. contact with H_3PO_4 (98%) enriched with D; almost no D-H exchange was observed with this cyclic ketone and a similar result was obtained in a similar treatment of the initial dicarbonyl. The latter (14.4 g.) was then treated with D_2PO_4 prepd. from 9.6 g. P_2O_5 and 4.4 g. D_2O , 8 hrs. at 20-1°, yielding I contg. 1 D atom per mol. This was ozonized yielding HCO_2H and higher org. acids, the latter yielding cryst. α -deutero- α -isopropyl- β , β -dimethylsuccinic acid, m. 48°. Oxidation of this with $\text{Br}-\text{H}_2\text{O}$ gave α -deutero- α -isopropyl- β , β -dimethylsuccinic acid, m. 134-5°, which retained the same amt. of D as the cyclic ketone. A mechanism for the cyclization is presented which is consistent with the exptl. results. G. M. Kosolapov

(2)

KURSANOV, D. N.

AID P - 1118

Subject : USSR/Chemistry
Card 1/1 Pub. 119 - 1/5
Authors : Kursanov, D. N. and Voyevodskiy, V. V. (Moscow)
Title : Some new data on hydrogen exchange between organic radicals and ions
Periodical : Usp. khim., 23, no. 6, 641-653, 1954
Abstract : Hydrogen exchange of free organic radicals and of organic cations is reviewed. Experimental data on the hydrogen exchange of carbonyl compounds with D₂SO₄ are compiled in a table. One table, 38 references (19 Russian: 1934-54).
Institution : None
Submitted : No date

Reactions of hydrogen exchange of saturated ketones with acids. D. N. Kursanov and V. N. Setkina (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 94, 69-72 (1954).—D-H exchange was studied in the series of satd. aliphatic ketones in media containing H_2SO_4 and H_3PO_4 enriched with D. The following extents of exchange, reported as percentages of exchange of all α -H atoms in the ketones, were found: in D_2SO_4 , MeCOBu 89.5, cyclopentanone 102.9, cyclohexanone 83.5; in D_3PO_4 , MeCOBu 100.3, cyclopentanone 104.9, cyclohexanone 100.0. The proof that the exchanged D atoms were located in α -positions was had by treatment of the D-exchanged ketones with $2Zn$ yielding the dibenzal derivs, which were devoid of D content. The reactions in D_2SO_4 were run 1 hr. at room temp., those in D_3PO_4 for 48 hrs. at room temp. Cf. C.A. 47, 851f. G. M. Kosolapoff.

KURSANOV, D. N.

USSR/Chemistry

Card : 1/1

Authors : Lavrushin, V. F., Kursanov, D. N., Memb. Corres. of Acad. of Sc. USSR.;
and Setkina, V. N.

Title : Reaction of saturated hydrocarbons with sulfuric acid

Periodical : Dokl. AN SSSR, 97, Ed. 2, 265 - 266, July 1954

Abstract : Experiments showed that saturated hydrocarbons absorb light in the range of very short waves thus indicating that the curves of their sulfuric acid solutions owe their origin to hydrocarbon-sulfuric acid reaction products. Since the absorption curves of hydrocarbons are analogous to each other and with the absorption curves of trimethylcarbinol it becomes evident that the nature of their reaction with sulfuric is also identical. It was also proven that the particles, forming during the reaction of hydrocarbons with sulfuric acid, are identical. Six references. Graph

Institution : Acad. of Sc. USSR, Inst. of Element. - Organic Compounds and the A. M. Gorkiy State University, Kharkov

Submitted : March 24, 1954

KURSANOV, D.N.

USSR/Chemistry - Physical chemistry

Card 1/1 : Pub. 22 - 21/48

Authors : Kurasnov, D. N., Memb. Corresn. of Acad. of Sc. USSR.; Setkina, V. N.;
and Bykova, E. V.

Title : About the intra-molecular effect of positive-charged centers on the
proton mobility of H-atoms

Periodical : Dok. AN SSSR 97/5, 835-838, August 11, 1954

Abstract : The effect of positive-charged centers on the proton-mobility of hydro-
gen atoms, is explained. The difficulties involved in studying the
effect of a tri-covalent positive charged (oxonium) O-atom on the pro-
ton activity of H-atoms, are discussed. The results of the hydrogen
interchange reactions are shown in tables. Four references: 3-USSR
and 1-German (1933-1954).

Institution : ...

Submitted : April 8, 1954

KURSANOV, D. N.
USSR/ Chemistry - Elementorganic compounds

Card 1/1 Pub. 22 - 21/40

Authors : Parnes, Z. N., and Kursanov, D. N., Memb. Corresp. of Acad. of Sc. USSR

Title : Effect of substitutes on the mobility of hydrogen atoms of unsaturated and aromatic ketones

Periodical : Dok. AN SSSR 99/2, 265-268, Nov 11, 1954

Abstract : Experiments were conducted to determine whether the nature of the R radical in ketones has any effect on the mobility of hydrogens of the methyl group oriented opposite the carbonyl group and whether the conjugations of the R radical and methyl group with the carbonyl group are independent from each other. It was found that the nature of the radical in ketones has a definite and essential effect on the mobility of the hydrogen atoms in the methyl group. The rate of the hydrogen exchange increases with the increase in the electron-acceptor characteristics of the R radical. The effect of the ethylene (or aromatic) bond in alpha, beta position, relative to the carbonyl group on the hydrogen atom mobility in the case of an alpha-carbon atom oriented on the other side of the carbonyl group, is elucidated. Two USSR references (1949 & 1953).
Tables

Institution : Acad. of Sc. USSR, Institute of Elementorganic Compounds

Submitted : June 18, 1954

Kursanov, D. N.

USSR/ Chemistry - Analytical chemistry

Card 1/1 Pub. 22 - 32/63

Authors : Setkina, V. N.; Plate, A. F.; Sterligov, O. D.; and Kursanov, D. N., Memb. Corres. of Acad. of Sc. USSR

Title : Possibility of adapting the hydrogen exchange reaction for the analysis of saturated hydrocarbon mixtures

Periodical : Dok. AN SSSR 99/6, 1007-1010, Dec 21, 1954

Abstract : The characteristics of hydrogen exchange reaction and the possibility of applying this reaction for analytical purposes were investigated. A compulsory condition for the adaption of the hydrogen exchange reaction for the analysis of saturated hydrocarbon mixtures was found to be the attainment of reaction equilibrium. It was established that the hydrogen exchange reaction of aliphatic and alicyclic hydrocarbon mixtures containing from 5 to 7 carbon atoms in the molecule begins within a period of 10 - 20 hrs. The results, obtained during the reaction of two-component saturated hydrocarbon mixtures, are tabulated. Nine USSR references (1935-1954). Tables.

Institution:

Submitted: June 18, 1954

Kursanov, D. N.

Exchange reactions and cleavage in the group of quaternary ammonium salts. IX. Reaction of quaternary ammonium salts with secondary and tertiary alcohols. V. N. Setkina, N. K. Baranetskaya, and D. N. Kursanov. (Inst. Hetero-org. Compounds, Acad. Sci. U.S.S.R., Moscow).

Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1955, 750-5; *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1955, 667-72 (Engl. translation); cf. *C.A.* 46, 458h. Quaternary ammonium salts contg. the ROCH_2 group react with secondary and tertiary alcs. with formation of formals. Thus, cyclohexyloxymethylpyridinium chloride (I) (30.84 g.) and 13.47 g. cyclohexanol after 6 hrs. at 100° gave 18 g. $(\text{C}_6\text{H}_{11}\text{O})_2\text{CH}_2$ (II), b_p 279-80°, d_4^{25} 0.9716, n_D^{25} 1.470. *sec*-Octyloxymethylpyridinium chloride (IIIa) and *sec*-octyl alc. gave 46% $(\text{C}_{11}\text{H}_{23}\text{O})_2\text{CH}_2$ (III), b_p 152.5-3°, d_4^{25} 0.8419, n_D^{25} 1.4322. I and MeEtCHOH gave 24.9% $(\text{MeEtCHO})_2\text{CH}_2$, b_p 60.5-60.8°, d_4^{25} 0.8472, n_D^{25} 1.4124, 52.9% $\text{MeEtCHOCH}_2\text{OC}_6\text{H}_{11}$, b_p 99.5-101°, b_m 0.9078, n_D^{25} 1.4402, and 22.2% II. I and *iso*- PrOH gave 18.4% $(\text{iso-PrO})_2\text{CH}_2$, 52.2% *iso*-

$\text{PrOCH}_2\text{OC}_6\text{H}_{11}$, b_p 70-70.5°, d_4^{25} 0.9089, n_D^{25} 1.4370, and 29.4% II. Isopropoxymethylpyridinium chloride and MeCOH gave 38.4% *iso*- $\text{PrOCH}_2\text{OCMe}_2$, b_p 71.1-1.5°, d_4^{25} 0.9223, n_D^{25} 1.3630, 40.6% $(\text{iso-PrO})_2\text{CH}_2$, and 21% $(\text{MeCO})_2\text{CH}_2$, b_p 77-9.5°, d_4^{25} 0.8300, n_D^{25} 1.3982. IIIa and MeCOH in 17 hrs. at 120° gave 8.9% $(\text{MeCO})_2\text{CH}_2$, 48% $\text{MeCOCH}_2\text{OCHMeC}_6\text{H}_{11}$, b_p 128-9°, d_4^{25} 0.8551, n_D^{25} 1.4204, and 43.1% III. I and *tert*- AmOH in 16 hrs. at $110-15^\circ$ gave II and $\text{C}_{11}\text{H}_{23}\text{OCH}_2\text{OCMe}_2\text{Et}$, b_p 119.5-20.5°, d_4^{25} 0.9103, n_D^{25} 1.4453, in combined yield of 26%. $\text{C}_{11}\text{H}_{23}\text{CHMeOCH}_2\text{Cl}$ b_p 98-9°, d_4^{25} 0.9240, n_D^{25} 1.4357.

G. M. Kosolapoff

Application of the Ball reaction on aromatic alcohols. I. Shirochiko Sugasawa and Kitaro Mizukami (Univ. Tokyo). *Pharm. Bull. (Japan)* 2, 341-2 (1954).—Ball's method (cf. *et al.*, *C.A.* 42, 6916f) for oxidizing polyene alcs. in Et_2O with activated MnO_2 to unsatd. aldehydes was applied to aromatic alcs. with the following results (alc., reaction temp., reaction time in hrs., and % yield and m.p. of the semicarbazone of the corresponding aldehyde given): $\text{Ph-CH}_2\text{OH}$, 22-35°, 2, 70, 215-16°, 3,4- $\text{CH}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}$, 35°, 1, 65, 177°, 2- $\text{HO-C}_6\text{H}_4\text{CH}_2\text{OH}$, 20°, 3, 60, 224°, furfuryl, 19-20°, 3.5, 40, 190-3°, 3-pyridyl, 21°, 1.5, 50, 213-14° and 4-pyridyl, 35°, 3, 60, 213-15°. W. T. S.

PM

KURSANEV, D.N.

48

Reaction of 1-apocamphancarboxylic acid with hydrazine
 acid. D. N. Kursanev and S. V. Vili. Zhur. Obshch.
 Khim. 25, 2609-2610 (1951). Preparing 6.2 g ketone and
 with 10 ml. triethylene glycol, 0 g. NaH, H₂O and 1 g
 powdered KOH, with gradual distn. of H₂O and excess NaH,
 maintaining the bath temp. at 105° and finally at 102° 1.5
 hrs. yielded after cooling and acidification with H₂SO₄ 8.0 g
 1-apocamphancarboxylic acid, m. 117-18°. This (4.0 g.)
 in 25 ml. CCl₄ and 15 ml. conc. H₂SO₄ was treated with
 2.25 g. NaH over 6.5 hr. at 35-40° after 1 hr. at 30° the
 mixt. was treated with conc. acid with CCl₄ and the
 layer steam distd. after adding of NaOH, boiling at 100°
 1-apocamphylamine, m. 173-74° (recryst. m. 174-175°).
 m. 121-2° (lit. Bartlett and Knox, C.A. 34, 4009). No by-
 products were formed in the Schmidt reaction. C. M. K.

RM

Kursanov, D. N.

Reactions of hydrogen exchange of aldehydes. D. N. Kursanov and Z. N. Parnes. Doklady Akad. Nauk S.S.S.R. 109, 817-8 (1955). D-H exchange was studied in several aldehydes in dry dioxane treated with D₂O in the presence of N,N'-dimethylpyrrolamine catalyst at 100° in sealed ampuls. The % exchange found in 50 hrs. was enanthaldehyde 96, cyclamenal 92, BzH 1, PhCH:CHCHO 2, citral 70, MeCCHO 0.5, and jasminaldehyde 5. The exchange takes place with the H atoms of the Me and methylene groups at the γ -C atom in unsatd., and at the α -C atom in satd. compds. (Cf. C.A. 48, 10549c). G. M. K.

2/

Chau

MD

KURSAV, D.N.

7

Reaction of hydrogen exchange in saturated carboxylic acids with sulfuric acid-d₂. V. N. Selezina, E. V. Bykova, and D. N. Kursav (Inst. Inorganic Compds., Acad. Sci. USSR, Moscow). Dokl. Akad. Nauk SSSR 101: 240-241 (1955). The following percentages of H-D exchange took place between carboxylic acids and D₂SO₄ in the indicated number of hrs. (in parentheses): *iso*-PrCO₂H (110) 82%, (185) 94%, (260) 91%; EtCHCO₂H (120) 102%, (310) 89%; *iso*-PrCH₂CO₂H (120) 100%, (310) 91%; *iso*-AmCO₂H (180) 94%, (214) 87%; *iso*-AmCH₂CO₂H (240) 49%, (2520) 89%; Me₃CCO₂H 0%. The exchange takes place only with H atoms on the α-C atom and the extent of exchange is equal to the total no. of α-H atoms available. No exchange took place with acids having H atoms in the α-position. The mechanism of exchange is discussed briefly.

DM 226

KURSNOV, D.N.

8

Reaction of hydrogen exchange of saturated hydrocarbons with one and several tertiary carbon atoms and sulfuric acid: D. N. Kursnov, V. N. Setkina, and A. P. Meshcheryakov (Inst. Hydrocarb. Compds., Acad. Sci. U.S.S.R., Moscow).

Chem Doklady Akad. Nauk S.S.S.R. 165, 279-81 (1955); *ibid.* C.A. 47, 851f. H-D exchange of several branched hydrocarbons with D_2SO_4 was studied in exposures up to 10.5 hrs. n-Octane gave 1.8-2% exchange; 3-methylheptane 100.1%; 2,3,4-trimethylpentane 88-9% exchange. Exchange of 3-methyl-3-D-heptane with H_2SO_4 resulted in considerable enrichment of the acid with D and a corresponding loss of D by the hydrocarbon. The labeled hydrocarbon was prep'd. by dehydration of 3-hydroxymethylheptane over Al_2O_3 at 400° , yielding mixed octenes which with HCl gave 3-chloro-3-methylheptane, b_p 46.5-6.8°, d₄ 0.8773, n_D 1.4322, which was converted to RMgCl and this decomp'd. with D_2O ; 3-methyl-3-D-heptane was dist'd. and purified by chromatography on SiO_2 ; the product used had n_D 1.3982. The exchange reactions were run in a shaker at room temp.

G. M. Kosolapoff

DM

KUDRYAVTSEV, R.V.; OTTESEN, B.V.; KURSANOV, D.V.

Determination of oxygen isotope content in organic compounds.
Kudriavtsev, Zhur.ob.khim. 26 no.4:1035-1039 Ap '56. (MLRA 9:8)
(Oxygen--Isotopes)

KURSANOV, D.N.

Hydrogen exchange of carbonium ions with acids and hydrogen exchange
of carbonyl compounds with deuterium oxide in an alkaline medium.

Ukr.khim.zhur. 22 no.1:34-37 '56.

(MLRA 9:6)

(Hydrogen) (Carbon compounds)

KURSANOV, D. N.

USSR/ Physical Chemistry - General Problems on Isotope Chemistry B-7

Abs Jour : Referat Zhur - Khimiya, No 3, 1957, 7414

Author : Kudriyavtsev, R.V., Ottesen, B.V., and Kursanov, D.N.
 Title : Determination of the Isotope Composition of Oxygen in Organic Compounds

Orig Pub : Zh. ogshch. khimii, 1956, Vol 26, No 4, 1035-1039

Abstract : A method is described for the destructive hydrogenation of organic substances for the purpose of determining the isotope composition of the oxygen in these substances; the hydrogenation is carried out at 300° in an H₂ atmosphere and over a Ni catalyst. At 300-400° there is no exchange between the walls of the tube, made of Mo-glass, and H₂O¹⁸. The catalyst contains oxygen which can be exchanged with the water vapor. In order to establish the equilibrium for this exchange four passes of vapor over the catalyst at 300° are sufficient. The error in the determination is 3-4 percent.

Card 1/2

- 70 -

USSR/ Physical Chemistry - General Problems on Isotope Chemistry B-7

Abs Jour : Referat Zhur - Khimiya, No 3, 1957, 7414

The method cannot be used with substances which contain S, P, halogens, and other elements which will poison the catalyst, nor with substances which boil above 200°.

Card 2/2

- 71 -

KURSANOV, D.N.; KUDRYAVTSEV, R.V.

Study of the hydrolysis mechanism with the aid of a heavy oxygen isotope. Part 1. Hydrolysis of ethyl propionate in an alkaline medium. Zhur.ob.khim. 26 no.4:1040-1041 Ap '56. (MLRA 9:8)
(Hydrolysis) (Oxygen--Isotopes) (Propionic acid)

MR. A. NOV. D. H.

Synthesis of ethyl alcohol containing heavy metal
 catalysts. J. V. ~~_____~~
 October 14, 25, 1944 - 10/14/44
 ACH-vapor passed through an activated
 ionating column containing ethyl alcohol
 gave ACH conty. 1.08-1.1% (approximately 1% of
 of 0.4) which passed over Raney Ni
 RORH. b.p. 78-81°C. at 1.56 mm.

Rm 7

KURSAV, D. N.

Study of the mechanism of hydrolysis by means of heavy oxygen isotope. II. Hydrolysis of dimethyl sulfate in acid and alkaline media. D. N. Kursav and R. V. Kudryavtsev. Zhur. Obshch. Khim. 28: 2087-2090, 1954; cf. C.A. 50, 14038d; Lander and Green, C.A. 53, 1778c. Heating Me₂SO₄ with aq. NaOH in H₂O contg. 1.2% O¹⁸ with continuous distn. of MeOH, gave MeOH contg. 0.82% O¹⁸, when a small amt. of aq. soln. was used, whereas with large excess of aq. soln. the MeOH obtained had 1.16% O¹⁸. Heating Me₂SO₄ with H₂O contg. a trace of H₂SO₄ gave MeOH contg. 1.8% O¹⁸ and some MeOH contg. 1.01% O¹⁸. The results indicate that hydrolysis of Me₂SO₄ does not involve the S-O bond, but is directed only at the C-O link, in both acid and alk. solns. However, the content of O¹⁸ in the resulting MeOH is higher than in starting H₂O caused by exchange of O in the SO₃ group. This was confirmed by the higher content of O¹⁸ in the product obtained with large excess of H₂O.

R.M.M.T.

USSR/ Organic Chemistry - Theoretical and general questions
of organic chemistry

E-1

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11570

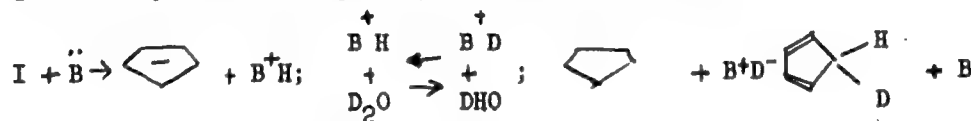
Author : Kursanov D.N., Parnes Z.N

Inst : Academy of Sciences USSR

Title : On Hydrogen Exchange Reaction of Cyclopentadiene:

Orig Pub : Dokl. AN SSSR, 1956, 109. No 2, 315-318

Abstract : All 6 atoms of H of cyclopentadiene (I), under mild conditions (20 hours, 20°, solvent: dioxane), in the presence of N, N'-dimethyl-alpha-pyridomimine, take part in the hydrogen exchange reaction (HER) with D₂O. Under these conditions sylvane and cycloheptatriene do not undergo HER. Pyrrole exchange only the H atom linked to N.



Ready occurrence of HER in the case of I is due to the stability of the cyclopentadienyl anion, having an aromatic nature, and the delocaliza-

Card 1/2

USSR/ Organic Chemistry - Theoretical and general questions
of organic chemistry

E-1

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11570

tion of the negative charge in the anion. The many times repeated establishment of acid-base equilibrium of delocalization of the negative charge results in complete exchange of H atoms (see scheme). In neutral and acid medium the HER of I does not occur. Ferrocene does not undergo HER with D_2O , which shows that the bond between Fe and cyclopentadienyl residue must be regarded as covalent .

Card 2/2

KURSANOV, D. N.

USSR/ Organic Chemistry - Theoretical and general questions
on organic chemistry

E-1

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11574

Author : Setkina V.N., Kursanov D.N.

Inst : Academy of Sciences USSR

Title : On Hydrogen Reactions of 1-Methylcyclohexanol-1 with Phosphoric
Acid

Orig Pub : Dokl AN SSSR, 1956, 109, No 3, 552-554

Abstract : A study was made of hydrogen exchange reaction (HER) of 1-methylcyclohexanol-1(I) with D_3PO_4 . I undergoes HER at $-5 - 0^\circ$. Content of D in I after the experiment was determined on the basis of excess density of water of I combustion and that of the combustion of methylcyclohexenes produced by dehydration of I with iodine. On HER of 1-methylcyclohexene-1 (II) under the same conditions, II is not hydrated to I and exchange of II is considerably lower than that of I, therefore HER of I does not take place with intermediate formation of cyclo-olefin. On the basis of these data, and also the data of cryoscopic and

Card 1/2

USSR/ Organic Chemistry - Theoretical and general questions
on organic chemistry

E-1

Abs Jour : Refeat Zhur - Khimiya, No 4, 1957, 11574

spectral investigation of solutions of tertiary alcohols in H_2SO_4
the conclusion is arrived at, that I forms with D_3PO_4 a
carbonium ion which undergoes HER.

Card 2/2

Effect of nucleophilicity of an anion on the character of the bond in tropylum compounds. M. R. Vol'pin, I. S. Akhrem, and D. N. Kuznetsov. *Khim. Nisula i Prom.* 2, 356-7 (1967). The character of the bond between $C_6H_5^+$ and X^- depends on the nucleophilicity of the X^- ion, and may be the dissociation constant, K , of the respective acids. Then the transitions between ionic and covalent salts of $C_6H_5^+$ at present, are $K = 1.2 \times 10^{-4}$ (HNCO) and 7.8×10^{-4} (HCN). To reduce the range, compounds were synthesized with AcOH and BaOH. Both were covalent liquids (bp. 55-58° and 78-82°, resp.), sol. in nonpolar solvents. The covalency was also established by the ultraviolet absorption spectra and by the ease of hydrolysis in H_2O and NaOH to give oxides and the ease of bromination. Hydrolysis of C_6H_5CN in concd. HCl resulted in partial isomerism to form phenylacetic acid. Thus acids

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2 may

bromination. Hydrolysis of C_6H_5CN in concd. HCl resulted in partial isomerism to form phenylacetic acid. These acids with $K = 1.2 \times 10^{-4}$ give ionic salts and those with $K = (0.3-1.75) \times 10^{-4}$ ($BrOH$ and $AcOH$) give covalent deriva. This agrees with the results of Doering, *et al.* (*C.A.* 49, 8832a).
I. Benveniste

KURSANOV, D.N.; VITT, S.V.

On the mechanism of the alkylation of alcohols by N-trimethyl-
α-phenethylammonium iodide. Dokl. AN SSSR 113 no.3:607-609
Mr '52:1111 (MLBA 10:6)

1. Institut elementoorganicheskikh soedineniy Akademii nauk SSSR.
2. Chlen-korrespondent Akademii nauk SSSR (for Kursanov).
(Alkylation) (Phenethylamine) (Ammonium compounds, Substituted)

KURSANOV, D.N.; BARANETSKAYA, N.K.; SETKINA, V.N.

~~Interaction on benzylpyridinium chloride with lithium cyclopentadienyl.~~ Interaction on benzylpyridinium chloride with lithium cyclopentadienyl. Dokl. AN SSSR 113 no.1:116-119 Mr-Apr '57. (MIRA 10:6)

1. Chlen-korrespondent Akademii nauk SSSR (for Kursanov).
2. Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR.
(Pyridinium compounds) (Cyclopentadienyl)

Using the ^{13}C isotope of oxygen for studying the mechanism of alkali
co-etherification of carbon ethers. *Chem. Abstr.* 27 no. 6: 1686-1687
Jan 1987. (1987 10:57)

1. Institut d'etats chimicheskikh soedineniy Akad. N. S. Khokhlov
Moscow--USSR (ethers)

KURSANOV, D.N.; VITT, S.V.

Study of the mechanism of alkylation of phenols by N-trimethyl-
 α -phenylethylammonium iodide. Dokl. AN SSSR 113 no.5:1066-1069
Ap '57. (MLRA 10:7)

1. Chlen-korrespondent Akademii nauk SSSR (for Kursanov).
2. Institut elementoorganicheskikh soedineniy Akademii nauk SSSR.
(Alkylation) (Ammonium compounds, Substituted) (Phenols)

KURBANOV 10 H.

7. 5
New method of preparation of tropylium and methylenetropylium compounds? D. N. Kurbanov and M. P. Vol'min (Inst. Hetero-Cyc. Compd., Acad. Sci., Moscow). Doklady Akad. Nauk S.S.S.R. 113, 839-42 (1957); cf. Deering and Knox, C.A. 49, 8873a. — Photochem. reaction of C_6H_6 with CH_3N_3 (D. and K., C.A. 48, 616b) yielded cycloheptatriene (I) (contg. 5% MePh after fractional distn.), bp 118.3-7°, n_D^{20} 1.3228. This (0.08 g.) added with cooling to 2 ml. conc. H_2SO_4 , kept 10 days, then dil. with 1 vol. H_2O , and treated with chloroplatinic acid, gave 18% tropylium chloroplatinate. While nonoxidizing acids did not effect this transformation, CrO_3 , HNO_3 , H_2SO_4 , SO_2Cl_2 , and BF_3 also gave tropylium salts. Addn. of 0.91 g. I to 4.1 g. PCl_5 in 40 ml. CCl_4 resulted in a colorless ppt. after stirring 1 hr. and refluxing 15 min. this was sepd., washed with CCl_4 , and treated with cooling with 4 ml. H_2O . The flask was rinsed down with EtOH and the aq. EtOH layer tr. d. with a slight excess of 30% $HClO_4$, yielding 5% tropylium perchlorate. Addn. of chloroplatinic acid to the filtrate gave 10% tropylium chloroplatinate. When the reaction was run overnight without heating the total yield reached 60%. Tropylium chloride, mp. 97° (from MePh), its aq. soln. gave the tests for Cl^- and tropylium ion. Fractionation of MePh with CH_2N_3 gave a fraction, bp 136.9°, n_D^{20} 1.5114, contg. same 70% methylenetropylium. This treated with PCl_5 as above gave a ppt. of methylenetropylium, which was isolated as a yellow crystalline substance at 140°, the yield was about 50%. G. M. H.

Ph az

KURSAKOV D.N.

7
Mechanism of pinacolone rearrangement by deuterium
exchange study. D. N. Kursakov and Z. N. Faries (Inst.
Heteroorg. Compd., Acad. Sci. U.S.S.R., Moscow). *Dokl.
Akad. Nauk SSSR*, 27, 668-71 (1957).—Adding 100% D₂SO₄
with ice cooling to (Me₂COH)₂, keeping 1 hr. in the cold,
treating with NaHCO₃, and extr. with Et₂O, showed on iso-
topic analysis of the resulting product, b. 102-3°, either by
conversion to semicarbazone or oxidation to Me₂CCO₂H
(making allowance for leaching of D from Me groups dur-
ing neutralization), that the resulting compound was Me-
CCOCD₃; thus Me₂CCO₂H was free of D. Thus, during the

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action is practically irreversible

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KURSHON, D.W.

Distr: 4E4j/4E3d/4E2c(j)

Reaction of bromotropilidene with phosphorus pentachloride. M. E. Val'pin, I. S. Alkhus, and D. N. Kozlov (Inst. Heteroorg. Compd., Moscow). *Izv. Akad. Nauk S.S.S.R. Khim. Nauk* 1957: 763-1. Ultra-violet illumination of 0.11 mole CH_2N_2 in 4 l. PhBr until evolution ceased gave a product, b.p. 48-51°, contg. 69.4% bromotropilidene, as deid. by hydrogenation over Pt. This product (0.53 g.) and 1.32 g. PCl_5 stirred in CCl_4 5 hrs., filtered, and the solid taken up in H_2O , neutralized with Na_2CO_3 , and extd. with Et_2O gave 0.21 g. tropone, b.p. 165°. This is 1.0095 (cf. Dauben and Ringold, *C.A.* 43, 1675b). This hydroxytropilium bromide, decomp. 230°, λ (H_2O) 312 m μ , insol. in Et_2O , sol. in EtOH and H_2O . Heating 0.15 g. bromotropilidene with 0.76 g. PCl_5 in heptane 0.5 hr. and taking up the isolated ppt. in MeNO_2 gave with H_2PtCl_6 an orange hydroxytropilium hexachloroplatinate, $\text{C}_8\text{H}_7\text{O}_2\text{PtCl}_6$, also formed on similar treatment of tropene with H_2PtCl_6 . G. M. Kosolapoff

DM

KURSAKOV D. N.

SETEUNA, V.N.; KURSAKOV, D.N.; BYKOVA, Ye.V.

Carbonium ions in the hydrogen exchange reaction. Probl. kin. 1
kat. 9:234-241 '57. (MIRA 11:3)
(Carbonium compounds) (Hydrogen--Isotopes)

Most of the papers in this collection were presented at the Conf. on
Isotopes in Catalysis which took place in Moscow, Mar 31-Apr 5, 1956.

KURSANOV, D.N.; SETKINA, V.V.; VITT, S.V.; PARNES, Z.N.

Study of reaction mechanism by the hydrogen exchange method. Probl.
kin. i kat. 9:242-244 '57. (MIRA 11:3)

(Chemical reaction--Conditions and laws)

(Hydrogen--Isotopes)

Kursanov, D. N.

AUTHORS: Kursanov, D. N., Vol'pin, M. Ye., 62-11-12/29
Akhrem, I. S., Kachkurova, I. Ya.

TITLE: Curtius' (Kurtsius) Rearrangement in the Series of Isomeric
 Cycloheptatrienecarbonic and Norcaradienecarbonic Acids
 (Peregruppirovka Kurtsiusa v ryadu izomernykh
 tsikloheptatriyenkarbonovykh i norkaradiyenkarbonovoy
 kislot).

PERIODICAL: Izvestiya AN SSSR, Otdelenie Khimicheskikh Nauk, 1957,
 Nr 11, pp. 1371-1378 (USSR)

ABSTRACT: Here Curtius' rearrangement in the series of isomeric α -
 cycloheptatrienecarbonic-(I), (R = COOH), β -cyclohepta-
 trienecarbonic-(II) (R = COOH), γ -cycloheptatrienecarbonic
 -(III) (R = COOH) acids are systematically investigated.
 It is shown that the rearrangement takes place under the
 conditions here existing without an isomerization of the
 migrating hydrocarbon radical.
 For the first time here 1,3,5-, 1,3,6- and 2,4,6- cyclo-
 heptatrienylisocyanate, norcaradienylisocyanate, 1,3,5,-
 1,3,6, and 2,4,6-cycloheptatrienylurea, norcaradienylurea,
 N-phenyl-N'-1,3,5-, 1,3,6- and 2,4,6-cycloheptatrienylurea

Card 1/2

Curtius' (Kurtsius) Rearrangement in the Series of
Isomeric Cycloheptatrienecarbonic and Norcaradienecarbonic Acids. 62-11-12/29

as well as N-phenyl-N'-norcaradienylurea were produced synthetically. The absorption-spectra in the near ultra-violet area ($25000 - 50000 \text{ cm}^{-1}$) of 22 derivatives of the cycloheptatriene and norcaradiene were investigated. It is shown that in the series of norcaradiene-derivatives (IVR = COOH, COOCl, CONH₂, NCO) the three-termed cycle transfers the linking similar to a double bond. There are 5 figures, 1 table, and 14 references, none of which is Slavic.

ASSOCIATION: Institute for Element-Organic compounds of the AN USSR (Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR).

SUBMITTED: July 2, 1956.

AVAILABLE: Library of Congress

Card 2/2

KURSANOV, D.N.

AUTHORS: Vol'pin, M.Ye., Akhrem, I.S., Kursanov, D.N.

62-12-20/20

TITLE: Letters to the Editor (Pis'ma redaktoru)
New Reactions of Tropyli Salts (Novyye reaktsii soley tropiliya).

PERIODICAL: Izvestiya AN SSSR Otdeleniye Khimicheskikh Nauk, 1957, Nr 12.
pp. 1501-1502 (USSR)

ABSTRACT: It was shown that the salts of cycloheptatrienyl very easily alkylate the compounds with mobile hydrogen. Tropyli salts react with the same ease with various aliphatic aldehydes. Aliphatic and aromatic ketones when heated also enter into reaction with the salts of tropyli. The latter easily alkylates numerous aromatic compounds. Tropyli differs from the other simple esters by the fact that it alkylates the esters of β -keto acids, β -diketones, and β -dicarboxylic acids easily in the case of soft conditions. Thus, cycloheptatrienylacetone acid ester is formed with aceto acid ester. The tropyli salts easily attach themselves to the compounds with activated short bonds (like vinyl esters, cyclopentadiene, phenyl acetylene, and others). The reactions investigated offer new possibilities for the synthesis of the derivatives of cycloheptatriene and tropyli. There are 4 references, 3 of which are Slavic.

Card 1/2

Letters to the Editor. New Reactions of Tropyl Salts

62-12-20/20

ASSOCIATION: Institute for Elemental-organic Compounds AS USSR (Institut
elementoorganicheskikh soyedineniy Akademii nauk SSSR).

SUBMITTED: October 9, 1957

AVAILABLE: Library of Congress

Card 2/2 1. Tropyl salts-Reactions

USCOMM-DC-54782

KURSANOV, D.N.
KURSANOV, D.N., PARNES, Z.N.

Studying the mechanism of pinacolone rearrangement by means of
deuterium exchange. Zhur. ob. khim. 27 no.3:668-671 Mr '57.
(MIRA 10:6)

1. Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR.
(Pinacolone) (Deuterium)

Kursanov, D. N.

19
 Use of oxygen-18 in the study of the mechanism of alkaline transesterification of esters. R. V. Kudravin and D. N. Kursanov (Inst. ~~Chemical~~ ~~Compds.~~ ~~Moscow~~). ~~Zhur. Obshch. Khim.~~ 27, 1680-7 (1957).—Slow distn. of $\text{EtCO}(\text{O}^{18}\text{Et})\text{BuOH}$ mixt. in the presence of Na resulted in recovery of O^{18} in EtOH and none being found in the ester. Thus, the reaction proceeds through acyl-O fission, as does the hydrolysis. G. M. Kosolapoff

Distr: 4E41/4E2c(1)

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KURSHNOV, D.N.

~~VOL'PIN, M.Ye.; ZHDANOV, S.I.; KURSHANOV, D.N.~~

New tropilium salts. Tropilium ion polarography. Dokl. AN SSSR 112
no.2:264-266 Ja '57. (MIRA 10:4)

1. Chlen-korrespondent AN SSSR (for Kursanov). 2. Institut elemento-
organicheskikh soyedineniy i Institut fizicheskoy khimii Akademii
nauk SSSR.
(Cycloheptatrienyl)

Reaction of benzylpyridinium chloride with cyclopentadienylidene
D. N. Yakhontov, N. K. Butanetskaya, and
V. R. Setkina (Inst. Higher Org. Compounds, Acad. Sci.
Moscow). Dokl. Akad. Nauk S.S.S.R. 113, 116-10
(1967).—Treatment of 29.18 g. BuLi with 33.1 g. cyclopentadiene with cooling gave after standing 2 hrs. 71.9% C₅H₅Li, as detd. by carbonation. This, suspended in Et₂O was added to a similar suspension of 102.0 g. C₅H₅N·CH₂PhCl and stirred 20 hrs., after which the mixt. was treated with H₂O yielding a ppt. of 0.55 g. cumulat. (I), C₁₁H₁₁N, augmented by 12.14 g. from the Et₂O soln., the product is golden yellow, stable in air, sol. in Me₂CO, PhNO₂, CHCl₃, and pyridine; it decomp. above 180°. It dissolves in acid and is pptd. by bases. It takes up 5 moles H over Pt, indicating 5 doub. bonds, confirmed by iodine no. The hydrogenated product, C₁₁H₁₃N, forms a methiodide, decomp. 160-70°, and chloroplatinate, C₁₁H₁₃N·0.5H₂PtCl₆, decomp. 140°. The amine cannot be acetylated. I has a dipole moment of 9.7 D. The structure of I appears to be a bipolar ionic structure with a cyclopentadienyl ring on the 2-atom of pyridine, the N carrying a pos. charge and the dienylium ring a neg. charge. Q. M. Kosolapoff.
Some peculiarities of 2,6-dichloro derivatives of pyridine.
L. N. Yakhontov (S. Ordzhonikidze All-Union Chem.-Pharm. Research Inst., Moscow). Dokl. Akad. Nauk

424j

Some properties of 2,6-dichloro derivatives of pyridine.
L. N. Yakubovskiy (B. Dzhonikidze All Union Chem.
Pharm. Research Inst., Moscow). *Doklady Akad. Nauk
S.S.S.R.* 113, 1088-9 (1977).—2,6-Dichloropyridines do not
form perites or salts with mineral acids. 2-Chloro-4-
methyl-3-(2-chloroethyl)pyridine forms a moderately stable
HCl salt. 2,6-Dichloropyridines do not form quaternary
salts with MeI and do not form N-oxides; heating with
SeO₂ does not change these compds. while 3-(2-acetoxy-
ethyl)-4-methylpyridine is oxidized readily to 3-(2-acetoxy-
ethyl)isonicotinic acid, m. 155-6°. 2,6-Dichloro-3-(2-acetoxy-
ethyl)-5-methylpyridine is unchanged after many
hours of heating with SeO₂ in MePh or alone even at 250°. Heating 2,6-dichloro-4-methylpyridine acid with excess
SOCl₂ gave its acyl chloride which gave 91% Et ester.
G. M. Kosolapov

AUTHOR KURSA NOV D.N., Corresponding Member of the Academy
VOLPIN M.Ye.

TITLE A New Method For Production of Tropilium And Metatropilium Compounds.
(Novyy put'polucheniya soyedineney tropiliya i metatropiliya -Russian)

PERIODICAL Doklady Akademii Nauk SSSR, 1957, Vol 113, Nr 2, pp 339-342 (U.S.S.R.)
Received 6/1957 Reviewed 7/1957

ABSTRACT At present two fundamentally different ways of producing the 7-term aromatic tropilium-system are known: 1.method: tropilium-dibromide (including small quantities of salts of the carbonyl-tropilium) is obtained by separating HBr dibromal cycloheptadiene. 2.method: This method is based on the slight isomerization of a norbornadiene-system into a tropilium-system. However, it would doubtlessly be interesting to investigate the possibility of a direct transition from the cycloheptatriene-system (IV) (tropilidene) with 3 double bonds to the aromatic tropilium-system. A conjugation of all of the six double bond- π -electrons must be possible which is realized in consequence of the separation in any way of a hydrogen atom together with an electron pair from the CH_2 -group of the cycloheptatriene and then at the same time the transition of the 7th carbon atom from the sp^3 -hybridization condition into the sp^2 - hybridization condition must be possible, which would lead to the formation of the aromatic tropilium-system. Here a nonbenzoid

Card 1/3

A New Method For Production of Tropilium And
Metatropilium Compounds.

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20-2-27/67

aromatic system $\sigma\pi$ -electrons would develop. When studying this direct transformation from cyclopentadienes into tropilium salts the authors investigated the influence of a number of electrophilic reagents, strong acids, oxidation agents, haloid derivatives etc. on tropilium salts. On the occasion of an influence of concentrated sulphuric acid on cycloheptatrienes an exothermic reaction accompanied by formation of resin develops. However, a tropilidene oxydation together with formation of considerable quantities of tropilium salts (18%) takes place. Acids without any oxidizing properties (concentrated phosphoric acid, hydrochloric acid) do not lead to a formation of tropilium. Concentrated nitric acid reacts very turbulently with cycloheptatriene, and small quantities of tropilium develop. Other oxidation agents in acid media effect a slighter or stronger transformation of cycloheptatriene into tropilium (CrO_3 - 14%, SeO_2 - 7% yield of tropilium salt). Phosphorus pentachloride very slightly reacts with cycloheptatriene at normal room temperature. Tropilium chloride develops and PCl_5 is reduced to PCl_3 . This reaction can serve as a good preparation method for producing tropilium salts. It is better to prepare tropilium as a mere continuous, not very hygroscopic, not easily soluble perchlerate, chloroplatinate or iodide. The same

Card 2/3

A New Method For Production of Trepilium And Metatrepilium
Compounds.

20-2-27/67

method is applicable for the preparation of methyltrepilium salts (II, R=CH₃) by the influence of phosphorus pentachloride on methylcycloheptatriene. On the other hand neither phosphorus trichloride nor phosphorus tribromide is able to effect this transformation. Similar to the reaction with phosphorus pentachloride the other proceeds with suluryl chloride. 25% trepilium salt develop with considerable resinification. Thienyl chloride does not react with cycloheptatriene. In the experimental part experimental conditions are described in detail.
(With 6 citations from publications).

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Card 3/3

Institute for element-organic Compounds of the Academy of Science
of the U.S.S.R.
16.10.1956
Library of Congress

AUTHOR KURSANOV, D.M., corresponding member of the Academy of Science and VITT, S.V. PA - 3157

TITLE On the Mechanism of the Alkylation of Alcohols by N-Trimethyl- α -phenethylammonium iodide.
(Issledovaniye mekhanizma alkilirovaniya spirtov ^Liodistym N-trimetil- α -fenetilammoniyem - Russian)

PERIODICAL Doklady Akademii Nauk SSSR, 1957, Vol 113, Nr 3, pp 607-609, (U.S.S.R.)
Received 6/1957 Reviewed 7/1957

ABSTRACT The alkylation of methyl-, ethyl- and H-butyl alcohols was investigated with the optically-active salt of d-N-trimethyl- α -phenethylammonium. It was found that in all cases investigated the ethers obtained had no optical activity. It remained unclear, however, whether racemization takes place with alkylation or in the initial salt of ammonia as a result of heating with alcohol at high temperatures. In order to clear this up, reaction was carried out in such a manner that the d-N-trimethyl- α -phenethylammonium iodide did not enter into reaction as a whole. That part, which did not enter into reaction was then separated from the salt mixture by fractioned crystallization. It was found that the separated salt retained nearly its entire original optical activity, whereas the α -phenethylmethyl ether obtained showed no optical activity. From the data obtained it can be seen that the alkylation of alcohols with N-trimethyl- α -phenethylammonium takes place by the formation of α -phenethylcarbonium, i.e. in accordance with the asynchronous

Card 1/2

PA - 3157

On the Mechanism of the Alkylation of Alcohols by N-Trimethyl- α -phenethylammonium Iodide.

process. The experiments are described.
(With one table and three citations from Slavic publications)

ASSOCIATION Institute for Element-Organic Compounds of the Academy of
Science of the U.S.S.R.

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SUBMITTED

AVAILABLE

Card 2/2

KURSANOV, D.N.

AUTHOR KURSANOV D.N., Corresponding Member of the Academy 20-5-34/67
VITT S.V.
TITLE The Study of the Mechanism of Alkylation of Phenols by N-tri-
methyl- α -phenylethylammonium iodide.
(Issledovanniye mekhanizma alkilirovaniya fenolov iodistym
N-trimetil- α -fenetilammoniyom -Russian)
PERIODICAL Doklady Akademii Nauk SSSR, 1957, Vol 113, Nr 5, pp 1066-1069 (U.S.S.R.)
Received 7/1957 Reviewed 8/1957

ABSTRACT A number of research workers already studied the alkylation of
phenols and phenolate anions which contain a benzyl- or substi-
tuted benzyl radical. It was found that on the occasion of in-
teraction between chlorid-N-benzylpyridinium and phenol a mixture
of C- and O-alkylation products is produced. It ought to be belie-
ved that this reaction, like other alkylation processes previously
studied belongs to the heterolytic reactions of the substitution
of the Sn type. Phenol alkylation should develop either according
to the synchronous mechanism A or to the asynchronous mechanism B,
the latter including the intermediate formation of a free carbo-
nium ion. The authors investigated the interaction between iodine-
N-trimethyl- α -phenethylammonium and resorcin and fluoroglucin. Du-
ring heating of these phenols with ammonium salt a substitution
of the hydrogen atoms of the phenol kernel by α -phenethylradical
(C-alkylation reaction) takes place at 150° and more. The same al-
kylation of the two above phenols through the optically active N-

Card 1/2

The Study of the Mechanism of Alkylation of Phenols
by N-trimethyl- α -phenylethylammonium iodide. 20-5-34/67

trimethyl- α -phenethylammonium was carried out at 155-175° with an abundance of the corresponding phenol. If the reaction develops according to schedule A, the produced α -phenethylphenols must be optically active, in the other case (B), they must be inactive. It was found that the α -phenethylphenols are optically inactive and also the α -phenylpropion acid produced from their oxidation. Herefrom it may be concluded that in phenol alkylation ammonium decay first to the accompaniment of the formation of α -phenethylcarbonium. The latter reacts with phenol and therefore reaction develops according to (B). This was also confirmed by the reaction with deuterioresorcin instead of resorcin. Reactions, methods, yields, etc. are described in detail. (With 6 Slavic references).

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Card 2/2

Institute for Element-Organic Compounds of the Academy
14.11.1956
Library of Congress

20-6-27/59

AUTHOR:

KURSANOV, D.N., VITT, S.V.

TITLE:

The Study of the Mechanism of the Alkylation of Amines by N-Tri-Methyl- α -Phenylethylammonium Iodide.

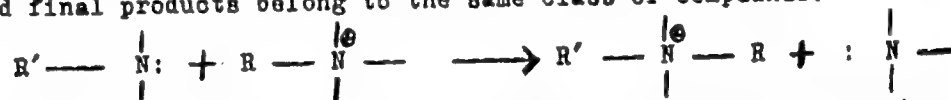
(Issledovaniye mekhanizma alkilirovaniya aminov yodistym N-tri-metyl- α -fenetilammoniem. Russian).

PERIODICAL:

Doklady Akademii Nauk SSSR, 1957, Vol 113, Nr. 6, pp 1283 - 1285 (U.S.S.R.)

ABSTRACT:

It is known that the ammonium salts of the type $Ar-CH_2-N^+(R)_3$ can alkylate primary and secondary amines by the transfer of the radical $ArCH_2$ from one nitrogen atom to the other. This process is also interesting by the fact that in this reaction the initial and final products belong to the same class of compounds:



The mechanism of this reaction remains uninvestigated. The authors investigated the alkylations of piperidine and morpholine by the optically active N-trimethyl- α -phenylethylammonium iodide. This reaction can develop either according to a synchronous or according to an asynchronous mechanism with an intermediate formation of a free carbanion. In the first case the developing N- α -phenylethyl-piperidin has to be optically active. In the second case (with car-

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The Study of the Mechanism of the Alkylation of Amines by N-Tri-methyl- α -Phenylethylammonium Iodide.

20-6-27/59

con ion formation) the optically activity would be lacking. It was found that in the substitution process this activity of the phenylethylradical is conserved: the N- α -phenylethylpiperidine obtained from the d-salt turned to the right side whereas the N- α -phenylethylmorpholine resulted from the l-salt turned to the left. Therefore the reaction passes according to a synchronous mechanism. It was necessary to determine the configuration of the leftturning substance. In so far as in the here applied reaction the asymmetrical centre is not concerned it can be stated that the leftturning substance belongs to the l-series. From this it results that in the case of the mentioned reaction with piperidine (and obviously also with morpholine) the inversion of the reversal of the α -phenylradical takes place. Since in the case of heating of longer duration optical purity was reduced, a secondary reaction of the symmetrical substitution seems to have taken place. Apparently the repetition of this process is bound to lead to ramification. In the experimental part the reactions with yields and constants are described in detail. (4 Slavic references).

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20-6-27/59

The Study of the Mechanism of the Alkylation of Amines by N-Tri-Methyl- α -Phenylethylammonium Iodide.

ASSOCIATION: Not given
PRESENTED BY:
SUBMITTED: 14 November 1956
AVAILABLE: Library of Congress

Card 3/3

KURBANOV, D. N., SETKINA, V. N., FARNES, S. N. and SYKOVA, Ye. V., (Inst. of Element-Organic Compounds AS USSR)

"Study of Several Heterolytic Reactions by the Hydrogen-Exchange Method." p. 13.

Isotopes and Radiation in Chemistry, Collection of papers of
2nd All-Union Sci. Tech. Conf. on Use of Radioactive and Stable Isotopes and
Radiation in National Economy and Science, Moscow, Izd-vo AN SSSR, 1958, 380pp.

This volume published the reports of the Chemistry Section of the
2nd AU Sci Tech Conf on Use of Radioactive and Stable Isotopes and Radiation
in Science and the National Economy, sponsored by Acad Sci USSR and Main
Admin for Utilization of Atomic Energy under Council of Ministers USSR
Moscow 4-12 Apr 1957.

KURSANOV, D.N.; VOL'PIN, M.Ye., kand. khim. nauk; PARNES, Z.N., kand. khim. nauk.

New aromatic systems. Report No.1: Tropylium cation and cyclopentadienyl anion as nonbenzene aromatic systems. Khim. nauka i prom. 3 no.2:159-173 '58. (MIRA 11:6)

1. Chlen-korrespondent AN SSSR (for Kursanov).
(Organic compounds)
(Cycloheptatrienylium compounds)
(Cyclopentadienyl)

KURSANOV, D.N.; BYKOVA, Ye.V.; SETKINA, V.N.

Hydrogen exchange in the process of heterolytic reactions. Exchange of hydrogen atoms during substitution of iodine in alkyl iodides. Izv. AN SSSR Otd. khim. nauk no.7:809-813 J1 '58. (MIRA 11:8)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Hydrogen) (Alkyl iodides)

5(3)

AUTHORS:

Kursanov, D. N., Parnes, Z. N., Kononova, R. G. SOV/62-58-12-18/22

TITLE:

The Case of a Retarded Hydrogen Exchange in the >N-H Group
(Sluchay zamedlennogo vodorodnogo obmena v gruppe >N-H)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1958, Nr 12, pp 1493-1494 (USSR)

ABSTRACT:

In this brief report the authors mention that the isotope exchange of hydrogen in the NH-group of dimethyl carbethoxy pyrrole takes place comparatively slowly. It turned out to be possible to measure the kinetics of this reaction at different temperatures. The velocity constants were calculated by a first order equation. The experiments were carried out at 12, 15, 20, and 25°. $K_{12} = 3.2 \cdot 10^{-5}$; $K_{15} = 5.6 \cdot 10^{-5}$; $K_{20} = 1.07 \cdot 10^{-4}$; $K_{25} = 2.21 \cdot 10^{-4}$ in sec^{-1} . Apparent activation energy = 25500 cal. The retarded hydrogen exchange which took place in this case is interpreted from the viewpoint of the theory developed by A. I. Brodskiy. There are 2 references, 1 of which is Soviet.

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The Case of a Retarded Hydrogen Exchange in the $>N-H$ Group SOV/62-58-12-18/22

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR
(Institute of Elementorganic Compounds, Academy of Sciences,
USSR)

SUBMITTED: May 22, 1958

Card 2/2

Kursanov D. N.

72-2-10/6

AUTHORS: Vol'pin, M. Ye., Akhrem, I. S., Kursanov, D. N.

TITLE: The Influence Exerted by the Nucleophilia of the Anion Upon the Nature of Linkage in Tropilium Compounds (Vliyeniye nukleofil'nosti aniona na kharakter svyazi v soedineniyakh tropiliya)

PERIODICAL: Zhurnal Obshchey Khimii, 1950, Vol. 28, Nr 2, pp. 330 - 333 (USSR)

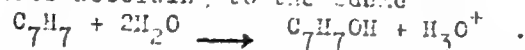
ABSTRACT: A number of salts of the aromatic 7-member cation of cycloheptatrienyl (tropilium) was recently produced (references 1 to 3). They are all salts of sufficiently strong acids ($X = Cl, Br, J, ClO_3, PtCl_6, B(C_6H_5)_4, HCO$). On the other hand the tropiliumoxide, methoxytropilium, tropilium cyanide, tropiliumthioether (references 1 and 2), where the X^- is an anion of sufficiently weak acids, are covalent compounds of type (II). Here and further the authors leave open the question whether the covalent tropilium derivatives possess a cycloheptatriene- or norcadiene structure (cf. reference 4). The authors made it their task to determine the boundary where the ionic compound $C_7H_7^+X^-$ transforms into the covalent compound C_7H_7-X . For this purpose they synthesized tropilium derivatives of acetic and benzoic acids ($K_a = 1.75 \cdot 10^{-5}$ and $6.5 \cdot 10^{-5}$). As well the tropilium acetate as the tropilium benzoate (more exactly the cycloheptatrienylacetate and -benzoate) proved to be typically covalent

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The Influence Exerted by the Nucleophilicity of the Anion Upon the Nature of Linkage in Tropilium Compounds

75-2-10/11

compounds - liquids - which can be solved in nonpolar solvents. Thus the transition from the ionic salts of tropilium to the covalent derivatives lies in the interval K_a of the corresponding acids. These results agree with the data by D ring, (reference 1) that the tropilium ion behaves in water like the acid $K_a = 1.3 \cdot 10^{-5}$ and reacts according to the scheme



The results obtained point to the assumption that the acids with $K_a > 1.2 \cdot 10^{-4}$ will yield ionic salts with tropilium; the acids $K_a \leq 1.3 - 1.75 \cdot 10^{-5}$ must yield covalent compounds with tropilium. This result is confirmed by the results of the interaction of tropilium chloride or tropilium perchlorate and cyclopentadienyl lithium. The formation of the covalent compound is explained by the weak acid properties of cyclopentadiene and consequently by the considerable nucleophilicity of the anion $C_5H_5^-$. The tropilium acetate and benzoate were synthesized by means of acylation of tropilium oxide (dicycloheptatrienylether) with corresponding acetic and benzoic anhydrides. This method of ether production may have quite a general importance. The attempts to produce tropilium acetate by means of an exchange reaction of tropilium perchlorate and potassium

Card 2/4

The Influence Exerted by the Nucleophilia of the Anion Upon the Nature of Linkage
in Tropilium Compounds

7-2-10/11

acetate in water and in alcohol were unsuccessful. Neither was it possible to produce tropilium benzoate by the exchange of potassium benzoate and tropilium perchlorate in water, nor by an exchange reaction of silver benzoate and tropilium bromide in alcohol or nitromethane. This indicates the instability of the cycloheptatrienyl ether and the inclination to hydrolysis. The covalent compound C_7H_7-X in tropilium cyanide and tropiliumcyclopentadienyl proved to be considerably stabler. It is interesting that in the acid process of the hydrolysis of tropilium cyanide a partial isomerization supposedly takes place and that phenylacetic acid is formed. Conclusions: 1) Tropilium acetate, -benzoate and cyclopentadienylcycloheptatriene which proved to be covalent compounds were produced. 2) It was shown that the nature of linkage of the cycloheptatrienyl residue with the anion depends on the nucleophilia of the anion. The transition from ionic to covalent tropilium derivatives lies in the range of K_a from $1.2 \cdot 10^{-4}$ to $1.3 - 1.75 \cdot 10^{-5}$. 3) It was shown that in the case of an acid hydrolysis of tropilium cyanide a regrouping with the formation of phenylacetic acid takes place. There are 6 references, 2 of which are Slavic.

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The Influence Exerted by the Nucleophilia of the Anion Upon the Nature of Linkage
in Propilium Compounds 79-2-10/61

ASSOCIATION: Institute for Elemental-organic Compounds AS USSR
(Institut elementoorganicheskikh sovedineniy Akademii Nauk SSSR)

SUBMITTED: April 15, 1957

AVAILABLE: Library of Congress

Card 4/4

AUTHORS: Setkina, V. N., Kursanov, D. N., Corresponding Member,
Academy of Sciences, USSR SOV/20-120-4-31/67

TITLE: Hydrogen Exchange Reactions of Alkyl Chlorides With Hydrochloric Acid and of Tertiary Butyl Alcohol When the Hydroxyl is Substituted by Chlorine (O reaktsiyakh vodorodnogo obmena alkilkhloridov s solyanoy kislotoy i tretichnogo butilovogo spirta pri zamene gidroksila na khlor)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 4, pp. 801-804 (USSR)

ABSTRACT: The reactions of tertiary aliphatic alcohols with a saturated HCl solution proceed very rapidly and practically irreversibly under the formation of alkyl chlorides. Reliable data on the mechanism of this reaction are lacking in publications. It might be assumed that the mentioned reaction proceeds according to the carbonium-ion-mechanism. The authors attempted to decide whether in connection with it an exchange of hydrogen takes place. They have found that the number of hydrogen atoms exchanged for deuterium corresponds only to the number of α -hydrogen atoms. For this purpose the reaction of tertiary

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SOV/20-120-4-31/67
Hydrogen Exchange Reactions of Alkyl Chlorides With Hydrochloric Acid and
of Tertiary Butyl Alcohol When the Hydroxyl is Substituted by Chlorine

butyl alcohol with a saturated HCl solution was investigated. The solution was enriched by deuterium. The rapidly formed tertiary butyl chloride contained only a small amount of deuterium. During a further contact between chloride and deuterio-chloric acid this amount increased (Table 1). Other tertiary chlorides behaved in the same way. A primary alkyl chloride, that is to say, butyl chloride did not enter the reaction under the same conditions (Table 2). Numerous investigations (Ref 4) of the mechanism of various solvolytic reactions of tertiary halide alkyls showed that all these reactions proceed according to the S_N1 -mechanism. Their velocity is determined by the ionisation velocity of tertiary halogenides. Obviously the mentioned reaction with deuterio-chloric acid is a special case of solvolytic monomolecular reactions. Thus it may be concluded that the initially mentioned hydrogen exchange reaction of tertiary alkyl chlorides is connected with their capability of being ionizable in a HCl solution which as is known has a high dielectric constant. The result of the ionisation of chlorides is their hydrogen exchange. The phenomenon that only α -hydrogen atoms of the

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30V/20-120-4-31/67

Hydrogen Exchange Reactions of Alkyl Chlorides With Hydrochloric Acid and
on Tertiary Butyl Alcohol When the Hydroxyl is Substituted by Chlorine

chlorides take part in this process can be explained by the impossibility of migration of the carbonium center along the hydrocarbon atom chain. This is impossible because of an electrostatic attraction of this center by anions or as a result of the influence exerted on the carbonium carbon by the solvate shell. In this reaction the carbonium ions are either not formed at all or they are so short-lived that they have not enough time to be exchanged for the acidous deuterium donors. The first assumption is more probable (Ref 5). There are 2 tables and 5 references, 1 of which is Soviet.

SUBMITTED: February 21, 1958

1. Hydrogen--Exchange reactions
2. Alkyl chlorides--Exchange reactions
3. Hydrochloric acid--Exchange reactions
4. Butancl--Chemical reactions
5. Chlorine--Chemical reactions
6. Substitution reactions

Card 3/3

AUTHORS: Kurganov, D. N., Bykova, Ye. V.,
Setkina, V. N. SOV/62-58-7-2/26

TITLE: Hydrogen Exchange in the Process of Heterolytic Reactions. Exchange of Hydrogen Atoms by the Substitution of Iodine in Alkyl Iodide (Vodorodnyy obmen v protsesse geteroliticheskikh reaktsiy. Obmen atomov vodoroda pri zameshchenii yoda v yodistykh alkilakh)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 7, pp 809 - 813 (USSR)

ABSTRACT: In the present paper the results obtained in the investigations of some reactions of the nucleophilic iodine substitution in alkyl iodide are described. The possibility of using the reaction of hydrogen exchange in the study of the mechanism of heterolytic reactions was investigated. Furthermore the hydrogen exchange was investigated in the following cases: a) In the hydrolysis of tertiary alkyl iodide by water enriched with heavy hydrogen (deuterium). b) In the exchange of iodine atoms in alkyl iodide with a 56% H J enriched with deuterium. It was found that the hydrogen exchange in C-H bonds occurs in such reactions where according to the data supplied by kinetic inves-

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Hydrogen Exchange in the Process of Heterolytic Reactions. Exchange of Hydrogen Atoms by the Substitution of Iodine in Alkyl Iodide

SOV/62-58-7-2/26

tigations they take place according to the monomolecular mechanism. It was shown in detail that the hydrolysis of tertiary iodides (C_4H_9J and $C_5H_{11}J$) and the iodide exchange in tertiary iodides are accompanied by hydrogen exchange reactions, if the hydrogen exchange does not take place in the reaction of the iodine exchange in secondary and primary iodides. This tends to show the bimolecular mechanism of these reactions. There are 2 tables and 30 references, 15 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elemental-organic Compounds, AS USSR)

SUBMITTED: February 5, 1957

Card 2/2

62-58-3-19/30

AUTHORS: Kursanov, D. N. , Baranetskaya, H. K.

TITLE: γ -Benzylpyridine-N=Cyclopentadienylide (γ -benzilpiridiniy-N-tsiklopentadiyenilid)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk , 1958, Nr 3, pp. 362 - 363 (USSR)

ABSTRACT: Three representatives of a new class of bipolar compounds (which contain a negatively charged cyclopentadienyl group) were already earlier described by the authors. It was now interesting to synthesize the above-mentioned compound, where (in contrast to the ilide) the ammonia nitrogen is directly connected with the negatively charged group. On that occasion the same method was employed which Lloyd and Smizum employed in the synthesis of piperidine-cyclopentadienylide. The compound synthesized by the authors of this report possesses all properties similar to the ilides (see the diagram on absorption in the ultraviolet spectral region. There are 1 figure and 5 references, 2 of which are Soviet.

Card 1/2

γ -Benzylpyridine-N-Cyclopentadienylide

62-58-3-19/30

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR
(Institute for ~~Elemental~~ organic Compounds, AS USSR)

SUBMITTED: October 12, 1957

Card 2/2

KURSANOV D. N.

79-2-28/64

AUTHORS: Parnes, Z. N., Vitt, S. V. , Kursanov, D. N.

TITLE: An Investigation of the Isomerization of Pinacoline by the Method of Traced Atoms (Issledovaniye izomerizatsii pinakolina metodom mechenykh atomov)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 2, pp. 410 - 413 (USSR)

ABSTRACT: At present different researchers found that the aliphatic carbon ions (iony karboniya) enter into a reaction of hydrogen exchange with acids. The hydrogen atoms are exchanged with the carbon atoms close to the carbon center (references 1 - 3). It was also shown that the carbon center of the carbon ion which was formed by the action upon carbonyl compounds by sulfuric or another strong mineral acid (at 0°C) is incapable of migrating, in contrast to the carbon ion which was obtained from the hydrocarbon with a tertiary carbon atom. Thus in the interaction of ketones, aldehydes, carboxylic acids with D₂SO₄ or D₃PO₄ the hydrogen exchange only takes place in those hydrogen atoms that are at C_α. But cases of ketone isomerization are known (references 4 - 7) which are explained by a displacement of the carbon center. Barton and Porter (reference 6) recently most exactly proved that the oxygen atom does not go over from one carbon to another in the ketone isomerization, but that

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79-2-23/64

An Investigation of the Isomerization of Pinacolone by the Method of Traced Atoms

only the hydrocarbon radicals migrate. For confirming this situation they used ditertiary butylketone (III) which contains C^{14} in the carbonyl group. It seemed interesting to the authors to investigate the interaction of pinacolone (V) with deuteriosulfuric acid under the same conditions under which the isomerization of the above-mentioned ketones (reference 6) takes place. The isomerization of pinacolone assumed in this connection cannot be determined by the usual chemical methods, as the reaction product is not different from the initial product; but by means of labelled atoms it was hoped to discover it. On the basis of data on the regrouping of pinacolone (reference 9) it must be reckoned with the fact that the ion (VII) either only exists for such a short time that it cannot markedly enter the hydrogen-exchange reaction and that the regrouping takes place synchronously, i.e. without forming a free ion (VII). But the ions (VI) and (VII) must easily enter the hydrogen reaction. Due to the reversability of the isomerization reaction all hydrogen atoms of pinacolone must finally be exchanged. On the basis of the data given it may be supposed that the hydrogen exchange in the hidden isomerization occurs as a consequence of a regrouping of methyl groups and is independent of the displacement of the carbon center. Summary: 1) The interaction of pinacolone with deuteriosulfuric acid was investigated under the conditions

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An Investigation of the Isomerization of Pinacoline by the Method of Traced Atoms

of the ketone isomerization. It was shown that under these conditions pinacoline exchanges the hydrogen atoms in the tertiary butyl group against deuterium. 2) The mechanism of the reaction of deuterio-exchange and pinacoline-isomerization were investigated. There are 1 table, and 9 references, 4 of which are Slavic.

ASSOCIATION: Institute for Elemental-organic Compounds AS USSR
(Institut elementoorganicheskikh soedineniy Akademii nauk SSSR)

SUBMITTED: January 16, 1957

AVAILABLE: Library of Congress

Card 3/3

SOV/ 20-120-3-26/67

AUTHORS: Kursanov, D. N., Corresponding Member, Academy of Sciences,
USSR, Volpin, M. Ye., Akhrem, I. S.

TITLE: The Reaction of Tropylium Salts With Vinyl Ethers and Mercury
 β -Chloroacetaldehyde (Reaktsiya soley tropiliya s vinilovymi
efirami i β -khlormerkuratsetal'degidom)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 3, pp. 531-534
(USSR)

ABSTRACT: A characteristic property of the stable aromatic cation of
cycloheptatrienylium (tropylium) is represented by its ca-
pability to react with nucleophilic reagents. (Ref 1). It
was to be expected that the electrophilic property of the
tropylium cation is sufficient also for a reaction with more
weakly nucleophilic reagents, as vinyl ethers. This actual-
ly was the case, as the tropylium salts react with simple
vinyl ethers in aqueous or alcohol solutions even in the
cold under a self-heating. This high reactivity is a result
of the influence of the electron-donor ether group. Compounds
with isolated or conjugated double bindings, however, without

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SOV-120-5-26/67

The Reaction of Tropylium Salts With Vinyl Ethers and Mercury β -Chloro-acetaldehyde

activating substances (as, for example, methylcyclohexene, cycloheptatriene and others), or with electron accepting substituents (cinnamic acid, acrylic acid, acrylonitrile, chloroallyl and others) do not react with tropylium salts under identical conditions. In all cases the same product results independent of the nature of the anion of the initial salt of tropylium (whether bromide or perchlorate) and independent of the character of the alkyl in the vinylalkyl ethers: cycloheptatrienyl acetaldehyde. This reaction is analogous to that of the addition of mercury salts to vinyl ethers (Ref 2). Therefore it could be assumed that the mechanism of interaction of the tropylium salts with vinyl ethers includes an attack upon the double binding of the vinyl ether by the ion $C_7H_7^+$. At the same time, or subsequently, an action of one molecule of the solvent (water or alcohol) takes place. an acetal or a semi-acetal is probably the intermediate product of the reaction. The reaction velocity with the tropylium salts is markedly reduced at the transition from the simple vinyl ether to the vinyl acetate. This apparently is connected with a partial withdrawal of electrons by the C=O group.

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SO720-120-3-26/67

The Reaction of Tropylium Salts With Vinyl Ethers and Mercury β -Chloro-acetaldehyde

Cycloheptatriene acetaldehyde was also obtained by a counter synthesis, that is to say by a reaction of the tropylium salts (bromide or perchlorate) with mercury β -chloroacetaldehyde. Because of an exchange of an Hg-atom with a tropylium radical an aldehyde was produced, which was identical with that produced from vinyl ethers. This is the first case to be investigated of an interaction of organomercury compounds with tropylium salts. The reaction of the tropylium salts with mercury β -chloroacetaldehyde proceeds according to the type of C-alkylation. The haloid acyls O-acylate mercury β -chloroacetaldehyde. There are 4 references, 3 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk
SSSR
(Institute of **Elemental-organic** Compounds AS USSR)

Card 3/4

The Reaction of Tropylium Salts With Vinyl Ethers and Mercury β -Chloro-
acetaldehyde SOV/20-120-3-26/67

SUBMITTED: January 14, 1958

1. Tropylium salts--Chemical reactions
2. Vinyl ethers--Chemical reactions
3. Mercury compounds (organic)--Chemical reactions

Card 4/4

SETKINA, V.N.; KURSANOV, D.N.

Hydrogen exchange reactions of alkyl chlorides and tertiary butyl alcohol, when hydroxyl is replaced by chlorine, with hydrochloric acid. Dokl. AN SSSR 120 no. 4:801-804 Je '58.

(MIRA 11:8)

1. Chlen-korrespondent AN SSSR (for Kursanov).
(Organic compounds)
(Hydrochloric acid)